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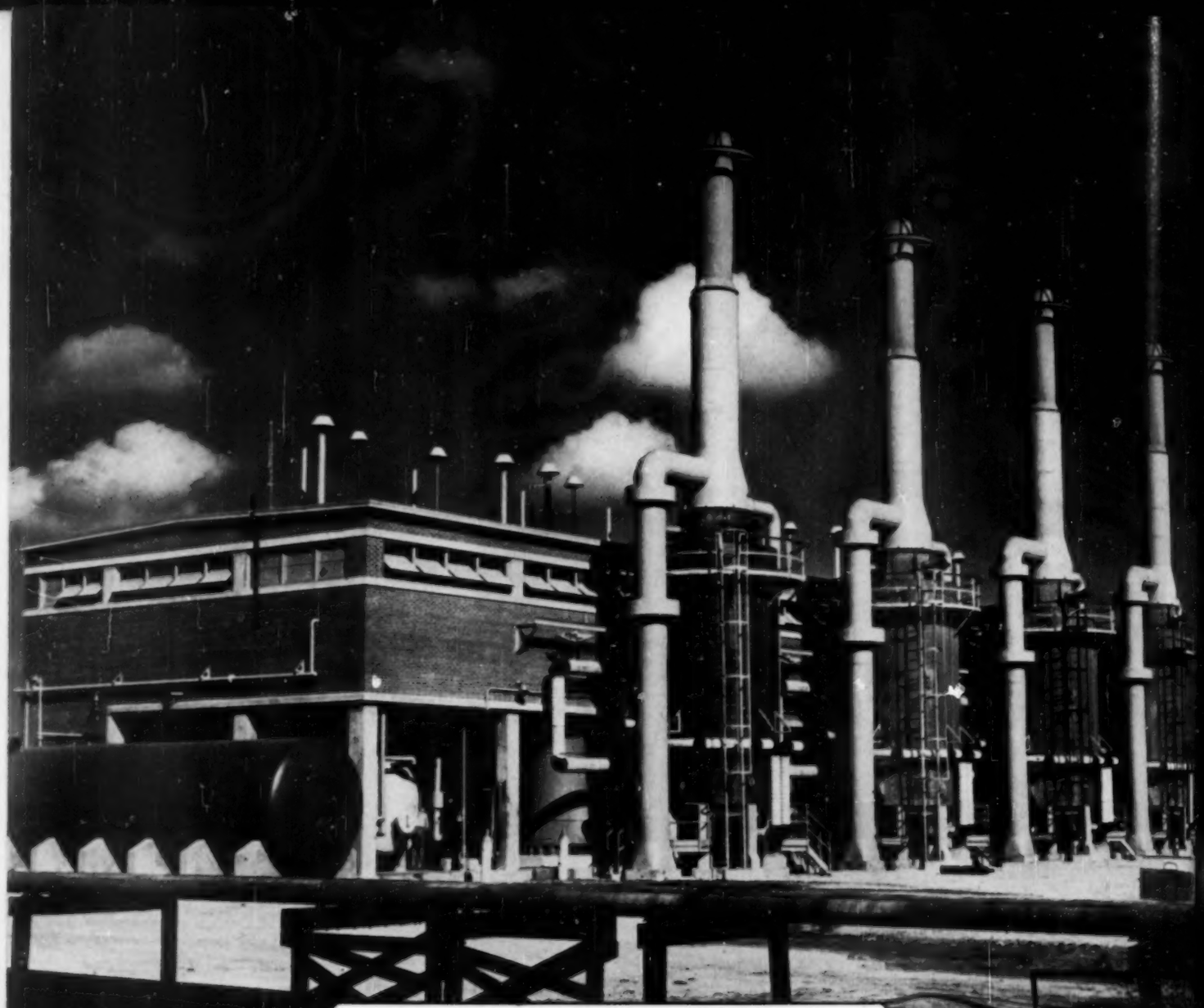
ELECTROCHEMICAL INDUSTRY

The Chemical Shore



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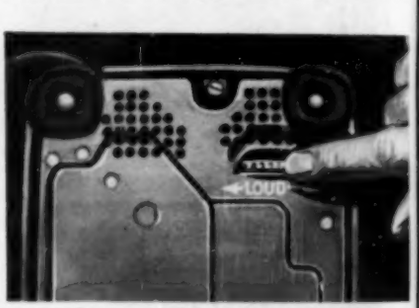

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Addition Agents for Negative Plates of Lead-Acid Storage Batteries

II. Pure Organic Compounds[1]

EVERETT J. RITCHIE

Research Laboratories, The Eagle-Picher Company, Joplin, Missouri

ABSTRACT

This paper presents some of the results of an experimental study of the effects produced by the addition of pure organic compounds to the negative active material of lead-acid storage batteries. The experimental conditions used in the study were selected to show large differences between compounds of similar structure or between members of a given series. These conditions have been described since they are not standard in the industry.

The results obtained at high discharge rates at 0°F (−17.8°C) have been grouped with respect to the chemistry and structure of the compounds tested. The effect of agent solubility, its electrolytic oxidation-reduction behavior, and the effect of structural isomerism are considered.

The effectiveness of pure organic compounds as expanders appears to be directly related to the ease with which they can be degraded to "humic substances." The best results were obtained with carbohydrates and some of the homologous phenolic compounds.

INTRODUCTION

The negative-plate addition agents used commercially as "expanders" to improve the low temperature, high rate discharge performance of a lead-acid storage battery have been naturally occurring materials or products obtained from them. Among these substances woodflour, cotton and hemp fibers, paper pulp, lignin sulfonic acids, and substances classed as humic acids have been most used.

Analytical studies of wood, various plant fibers, cellulose, lignin, and humic acid preparations have demonstrated the presence of a very large number of organic compounds containing many of the recognized organic structure groups or radicals. The primary objective of this work was the evaluation of the effect of the more common organic radicals as simple compounds and in some of their combinations with other radicals. Since the physical and chemical properties conferred upon an organic molecule by the introduction of a given radical into it may vary with the position taken by the radical, it was necessary to study and evaluate the several isomeric possibilities of a number of types of compounds. As far as possible the attempt was made to evaluate each compound as a member of a family rather than as an individual.

It was necessary to devise a test cell and a method of testing and reporting the data which would give a fair picture of the effect of the agents tested.

EXPERIMENTAL METHODS

The data reported in Table IV were not obtained under the usual test conditions applied to SLI storage batteries; hence, it is necessary to describe the conditions and the methods used so that the reader may be able to evaluate the data. The negative-plate area was reduced to about 50 per cent of its usual value in order to assure sufficient positive-plate capacity to discharge the negative plate at all temperatures. Instead of 300 amp discharge at 0°F (−17.8°C), the rate on these 50 per cent negative plates was cut to 100 amp which is equivalent to a 200 amp rate on a negative plate of normal area. By reducing the rate of discharge, the time of discharge was lengthened, and the variations in the results from different agents were spread out over a longer time interval. Instead of discharging the battery to a final cell voltage as a measure of the positive-plate capacity the cells were discharged to selected final negative-to-cadmium auxiliary electrode voltages.[2] The reported cell capacities were thus

[1] Manuscript received September 28, 1950. This paper prepared for delivery before the Buffalo Meeting, October 11 to 1[illegible] 1950.

[2] Hereafter abbreviated to N.C. voltage. As used herein a "very low N.C. voltage" means a large numerical negative value. Because the sign of the voltage measured between a cadmium auxiliary electrode and the negative electrode reverses during formation, or charge, the measured voltage decreases from an open-circuit voltage in the order of 0.17 v (in the plus direction), through zero to voltages as "low" 0.33 v (in the negative direction). This conven-

based entirely on negative-plate capacity. The details of cell construction, testing, and selection of addition agents follow.

Cell Construction

Negative plates.—The active material, composed of 1500 g milled mechanical furnace litharge, 7.5 g blanc fixe, 3.0 g lampblack, with addition agents in the test cells, was made into a paste with water and 1.325 sp gr sulfuric acid, and was hand pasted (on paper) at a paste density of 72 g/in.^{3} into conventional SLI grids of 0.090-in. (2.29 mm) thickness from which alternate rows of wires had been removed to reduce the net volume from 1.76 in.^{3} (28.8 cm^3) to very nearly 0.88 in.^{3} (14.4 cm^3) (Fig. 1). Because many of the addition agents would be lost by oven drying, the plates were treated instead by giving them a quick dip (about two seconds) in 1.250 sp gr sulfuric acid, using fresh acid for each addition agent. The plates were drained and air dried for at least 48 hours before assembly and formation.

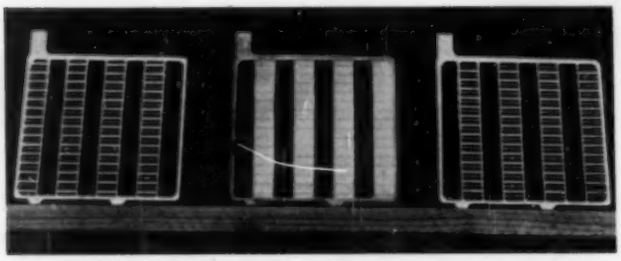

FIG. 1. Type of negative grids and plate used

Positive plates.—The active material was made from a blend of milled lead oxides containing 25 per cent red lead. Conventional SLI grids of 0.092-in. (2.34 mm) thickness and 2.00 in.^{3} (32.8 cm^3) net volume were hand pasted (on paper) at a paste density of 68 g/in.^{3} (4.15 g/cm^3), and the plates were dried in a humidity-controlled oven.

Formation.—Thirteen plate cells (7 negative, 6 positive) were assembled and separated using 0.078-in. (1.98 mm) thickness Port Orford Cedar separators. The assembled duplicate cells were formed in the end cells of three-cell glass jars which permitted some observation without disturbing the cell. Formation was carried out at 4.5 amp in 1.150 sp gr sulfuric acid until the negatives were formed. They were then removed and stored in distilled water, each pair of cells in a separate container. The formation of the positive plates was finished against dummy negatives. Nine pairs of cells were tested in each set.

tion is logical since the cell terminal voltage is the algebraic difference or spread between the N.C. voltage and the corresponding positive-to-cadmium voltage.

Assembly.—The formed duplicate groups were reassembled in the end cells of an S-8-D (100 amp-hr) container. The center cell had holes drilled in its outer walls to promote air and water circulation and was reinforced with a wooden block to prevent warping. The electrolyte was adjusted to 1.285 sp gr at 80°F (26.7°C) after charging at 6.0 amp until the gravity was constant plus one hour. This was also the criterion of charge used on all charges before and after measured discharges.

Cell Testing Discharge Conditions

Test schedule.—Data reported in this paper are those resulting from discharges at low temperatures to observe the effect of the addition agents, and discharges at a nominal 20-hour rate at 80°F (26.7°C) to show the base capacity of the plate. It is expected, other things being comparable, that a 120 amp-hr battery will have a higher low temperature capacity than would a 95 amp-hr battery; hence, the need of low rate discharge data to give information on the development of the active material. Table I gives the schedule of measured discharges upon which the reported data were based.

TABLE I. *Schedule of test discharge conditions*

Discharge Numbers		Amp rate	Temperature		Cut off voltages, N.C., v
Initial	Cycled		F°	C°	
1,4	61,64	100	0	−17.8	+0.80
2,5	62,65	3.5*	80	26.7	+0.30
3,6	63,66	100	80	26.7	+0.60

Cycles 7 to 60 inclusive were on automatic cycling.

* This value was selected to give a discharge of about 15 to 17 hours which was more convenient to use than the usual 20-hour rate.

TABLE II. *Control cell statistics*

	Minutes at 100 amp at 0°F		Hours at 3.5 amp		Formation amp-hr to final	
	Initial	Cycled	Initial	Cycled	final N.C.	N.C. v
Mean	4.2	4.2	15.7	16.6	118	−0.18
Avg dev.	0.47	0.59	0.51	0.54	8.5	0.02
Avg dev., %	11.2	14.0	3.2	3.3	7.2	11.1
Max dev.	1.5	1.4	0.7	1.3	18	0.13
Max dev., %	35.8	33.3	4.5	7.8	15.2	44.4

Reliability of results.—The significance of the results reported in Table IV for individual agents rests heavily upon the performance of the control cells tested at the same time. Table II gives data on the control cells of the study. It will be observed that, based on the average of two discharges, the 28 sets of control cells show a reasonably uniform capacity at the low discharge rate at 80°F (26.7°C). Since

the attempt had been made to control negative-active material weight, this was as expected. The much larger percentage variation and spread in the low temperature capacity results are in part due to the greater error involved in measuring a high rate discharge and to the greater effect of some variables that did not influence the low rate capacity. It was unavoidable that a few sets of negative plates aged for as much as two weeks before assembly and use, and this may have influenced their low temperature capacity. Although preventive precautions were taken, it is possible that traces of soluble addition agents entered the control cells during the checking of electrolyte and when using the auxiliary cadmium electrode. In several instances mechanical difficulties produced abnormally low results. Since each pair of control cells was treated exactly as the eight pairs of test cells teamed with it, any deviation from the normal schedule only affected the cells of that set. The statistical study shown in Table II indicates that variations in test cell capacities with different agents do not necessarily denote real differences unless they differ from these control cells by more than the average deviation of all control cells from the mean of all the control cells.

It was expected that a litharge-blanc-fixe-lampblack negative would lose capacity after about 60 cycles. At the cold rate about half of them did. The average capacity after cycling, however, was the same as the cold rate and a whole hour greater at the low rate under the test conditions.

The rather wide variation in final N.C. voltage on formation is probably due to temperature variations, and no attempt was made to finish formation at a constant temperature. The ampere-hours reported to a zero N.C. voltage were obtained by interpolations of frequent readings made throughout formation.

Selection and Calculation of Addition Agent Concentrations

Preference was shown for those compounds which had been identified in naturally occurring organic materials, or some of their more simple degradation products. The substances selected were members of homologous series or could be compared with other compounds of similar structure. Table III lists the organic groups tested, the classes of compounds in which they are found, and the formula weights used in calculating the amount of agent to use to obtain a constant active group percentage of 0.1 per cent. Compounds were also selected because of their having been mentioned in the patent literature (1, 2).

The addition agents were used in as pure a form as was obtainable. Most of them were purchased from the Eastman Kodak Company.

As an example of the method of calculating, consider the testing of propyl alcohol with a molecular weight of 60.07 and an active group weight of 29. The amount necessary to supply 0.1 per cent of $-\overset{|}{\underset{|}{C}}-OH$ to 1500 grams of negative material is $\frac{60.07}{29} \times 0.001 \times 1500$ or 3.14 grams which is 0.21 per cent based on the total agent weight.

TABLE III. *Organic radicals tested*

Organic structure group			Typical compounds
Formula	Name	Formula wt	
$-\overset{O}{\overset{\|\|}{C}}-OH$	Carboxyl	45	Acids
$-\overset{\|}{\underset{\|}{C}}-OH$	Carbinol	29	Alcohols (also used for phenols and naphthols)
$-\overset{O}{\overset{\|\|}{C}}-$	Carbonyl	28	Aldehydes, ketones
$-\overset{\|}{\underset{\|}{C}}-SH$	Mercaptan	45	Mercaptans, thiophenols, thionaphthols
$-\overset{\|}{\underset{\|}{C}}-NH_2$	Amine	28	Amines and amides
$2X(-\overset{O}{\overset{\|\|}{C}}-)$	Quinone	56	Quinone, naphthoquinones anthroquinones
SO_3H	Sulfonic acid	81	Aromatic sulfonic acids.

Experimental Results

In Table IV[3] a small part of the experimental data is given in condensed form. Capacities are reported in per cent of the performance of the control

[3] The complete Table IV has been deposited with the American Documentation Institute, 1719 N Street, N.W., Washington 6, D. C., from whom copies are available on either microfilm ($1.00) or photoprints ($1.35). Order document number 3841 directly from them. The complete Table IV contains data on 203 pairs of test cells studying 156 different organic compounds; it does not include data on the 28 pairs of control cells already discussed in Table II.

cells on the initial measured discharges. By "initial" is meant the average of discharges 1 and 4 at the cold rate and of 2 and 5 at the 3.5 amp rate at 80°F (26.7°C). By "cycled" is meant the average of discharges 61 and 64 at the cold rate and of 62 and 65 for the 3.5 amp at 80°F (26.7°C). Data are given for three commercial expanders tested under these conditions for comparison purposes.

The data are intended to supply answers to three questions pertinent to any study of battery addition agents: (*a*) Does the agent alter the properties of the active material to make it fragile, impermeable to the electrolyte, or difficult to form? (*b*) What is the initial effect of the agent upon the cold capacity before the electrolytic action of the battery has had opportunity to modify it? (*c*) What is the effect of the electrolytic action of cycling upon the agent?

The formation data were of value in screening out unsatisfactory agents. The "final" N.C. voltage appeared to be rather characteristic of a given agent, although subject to some variation with temperature and formation schedule.

The current required for the N.C. voltage to reach an arbitrary value, here selected as 0.0 volts, and expressed as a percentage of the current required by the control cells, was diagnostic of the nature of the formation taking place.[4] When only a small

ABRIDGED TABLE IV.[3] *Table (abridged) of relative capacities as influenced by various agents*

Agent	%	Capacity in % of initial control				Final N.C. formation voltage
		Cold rate		20-hour rate		
		Initial	Cycled	Initial	Cycled	
Acetic acid	0.13	104	104	93	95	−0.12
Benzoic acid	0.27	126	123	106	112	−0.18
o-Phthalic acid	0.19	110	105	100	101	−0.18
p-Phthalic acid	0.19	118	113	104	110	−0.15
α-Naphthoic acid	0.37	33	54	52	52	−0.28
Abietic acid	0.67	60	77	54	77	−0.33
Oleic acid	0.42	78	102	74	105	−0.29
Formaldehyde	0.10	118	89	101	94	−0.13
Propionaldehyde	0.21	100	80	97	91	−0.11
Benzophenone	0.65	76	90	91	104	−0.22
Ethyl alcohol	0.16	96	88	98	108	−0.19
Glycol	0.11	105	116	102	111	−0.18
Glycerol	0.11	113	132	105	109	−0.20
Arabinose	0.15	116	171	107	124	−0.18
Xylose	0.15	100	174	105	120	−0.20
Mannitol	0.18	110	177	107	124	−0.20
Sucrose	0.17	87	144	98	119	−0.21
Catechol	0.19	108	127	106	104	−0.16
Resorcinol	0.19	117	156	106	117	−0.16
Quinol	0.19	131	185	114	115	−0.16
α-Naphthol	0.50	173	290	96	118	−0.33
β-Naphthol	0.50	92	187	76	108	−0.25
Benzoquinone	0.19	162	225	115	129	−0.23
1-2 Naphthoquinone	0.28	107	122	69	110	−0.26
1-4 Naphthoquinone	0.28	132	100	94	72	−0.29
Anthraquinone	0.37	85	71	101	70	−0.27
α-Naphthol, 2 sulfonic acid	0.21	155	189	103	113	−0.22
α-Naphthol, 4 sulfonic acid	0.19	152	185	105	112	−0.19
α-Naphthol, 5 sulfonic acid	0.19	196	215	118	124	−0.16
β-Naphthol, 6 sulfonic acid	0.19	193	152	170	103	−0.14
β-Naphthol, 7 sulfonic acid	0.21	159	152	105	108	−0.15
β-Naphthol, 8 sulfonic acid	0.19	144	148	104	110	−0.15
Commercial neg. blends A		133	188	112	135	−0.24
Commercial neg. blends B		130	191	105	124	−0.22
Commercial neg. blends C		121	149	104	128	−0.24

[4] These values are included in unabridged Table IV.

amount of current was required, the final N.C. voltage frequently was of the order of −0.30 volts, and the initial capacities were low. With a number of agents, however, the N.C. voltage after dropping to a low value would slowly rise to a more normal final value. The explanation apparently lies in the effect of the agent upon the active material. If the product was difficult to wet, or if a definite impermeable surface film was present, the N.C. voltage read was largely due to the insulating surface. By repeated partial cycles this film could be formed and the N.C. voltage would rise toward a more normal value as the surface film was formed. Where incomplete formation had reduced the initial capacities, the low rate capacity was also effected, and after cycling a definite improvement was noted. Several hydroxy compounds which were most effective as expanders also interfered the most with the formation. The volatility of some of the agents influenced the results obtained with them by an undetermined amount.

The test data are in most instances for a single concentration of addition agent. With pure compounds, the expander effect appears to be sensitive to small changes in agent concentration and also to be much influenced by small variations in plate or cell preparation. Each separate compound could thus be made the basis for a study of concentration vs. preparation variables. The data of Table IV are, therefore, to be considered as indicating the possibilities, showing the relative value of the agents under the described conditions, rather than giving data obtained at optimum conditions. The more important radicals are discussed below and some of the more important relations are pointed out.

The carboxyl radical.—The aliphatic acids had very little effect upon the initial cold capacity, but many improved with cycling. Formic and oxalic acids, perhaps because of their reducing properties, had some beneficial action. The aromatic acids gave definite initial improvement but with cycling the effect was reduced and even detrimental.

A few of the acids produced the most fragile active materials of the entire study, giving plates that shed badly on formation and which also appeared to be water repellent. The high molecular weight acids such as stearic, undecylic, α-naphthoic, and abietic were among the poorest of all compounds tested but even these showed some improvement with cycling.

The results obtained with acetic acid, which showed it to have little effect although it is recognized as being deleterious, have not been satisfactorily explained. Perhaps since these tests were carried out on a strict time schedule and the cells were never allowed to stand idle in a discharged state, the expected acetic acid damage could not occur at the concentration tested.

Only a few of all the carboxyl-containing agents had an effect upon cold capacity of more than 20 per cent, either before or after cycling, and the maximum initial benefit was only 26 per cent. Although the carboxyl group is frequently present in expanders derived from natural products, it is evidently not the effective structural group in expanders producing the desired cold capacity improvement.

The carbonyl radical.—This radical is present in many natural substances because it is an intermediate product in the oxidation of primary and secondary alcohols and in the reduction of carboxyl groups. The group is also present in ring structures as quinones, and can also occur as a diketo structure. In many compounds a dynamic equilibrium exists between the keto form and its tautomeric enol isomer, an unsaturated alcohol. In aromatic compounds tautomerism is an important part of the explanation of the mechanism of oxidation of monosubstituted compounds to quinoid structures.

With so many different reaction possibilities, it was somewhat surprising to find that except for benzoquinone, all of the carbonyl compounds were ineffective as expanders. Without exception, the aldehydes tested gave better capacities initially than after cycling. Most of the ketones showed slight improvement with cycling but were still near the control cell level. Of the quinones the benzoquinone was very good initially and improved with cycling, while anthraquinone was poor to start with and got worse. The naphthoquinones were intermediate with the 1–2 form resembling benzoquinone, and the 1–4 isomer similar to anthraquinone with respect to the effect of cycling.

The conclusion may be drawn that the carbonyl group as an aldehyde may supply some initial expander action but that it is soon spent; as a ketone it is of little effect; and as a quinone it is of lasting benefit only when in certain special structures.

The carbinol radical.—The hydroxyl group is present in most natural materials used as expanders. Because the hydroxyl groups are formed, or introduced, as the result of both oxidation and reduction and also by hydrolysis and biochemical action, most plant substances contain complex structures in which the hydroxyl portion is a large percentage by weight. The complex polyhydroxyl compounds, such as the starches, sugars, cellulose, and lignin, have many reaction possibilities and have had long use as expanders.

The simple aliphatic alcohols are relatively stable and resistant to oxidation and reduction. It is not surprising that as addition agents they showed very little effect. The polyhydroxy aliphatic compounds

tested showed very little initial influence on cold capacity, but without exception they showed large gains after cycling. This is in qualitative agreement with practical experience using such compounds as expanders.

The aromatic and condensed ring hydroxyl compounds include those agents found to be of greatest effectiveness as expanders. Phenol itself was without significant initial effect, but a second hydroxyl gave a definite improvement related to the position taken and increasing in the order ortho, meta, para. This is also the order of increasing reducing properties. A third hydroxyl in either the vicinal or unsymmetrical positions produced no further improvement. All of the phenolic compounds improved with cycling. It is interesting that the meta and para dihydroxy benzenes after cycling should reach values of about the same order as the starting value for benzoquinone, which improved to a still higher value with cycling.

The hydroxy toluenes were much less effective than the hydroxy benzenes but all showed improvement with cycling. Only the orthocompound had an initial beneficial effect, the others were initially detrimental and their improvement with cycling was only to the control cell level. It is interesting that benzyl alcohol, which is isomeric with the cresols, should be definitely superior to the meta and para and equalled only by orthocresol.

The hydroxy naphthalenes were effective expanders but the active material was difficult to form. The best results were obtained when the hydroxyl group was in the alpha position. With two hydroxyls opposite (the 1–5 positions) the results were intermediate between those for a single hydroxyl group in the alpha and beta positions. Because of the formation difficulties it was not surprising that most of the naphthols should improve with cycling.

Since the hydroxy anthracenes are easily oxidized to anthraquinone, they were not tested. The hydroxy anthraquinones were all better than anthraquinone, and the 1-2-3 trihydroxy compound (anthragallol) was a good expander when properly formed.

The aromatic sulfonic acids.—The wide variation in results obtained when duplicate tests were made at different times demanded an explanation since the largest spread was obtained with the most effective agents. The cause appeared to lie in the way that the electrolyte wetted the surface of the plate. Many of the effective hydroxy derivatives seemed to produce a somewhat water-repellent active material.

It was assumed that the reaction between the addition agent, the leady material, and the pasting and dipping acid had resulted in an insoluble and nonporous active material, at least on the surface of the plate. Repeated partial cycles would form them eventually, but such procedure could never be put into practice and the operator was never quite certain that the process was complete. The problem was that of finding more soluble derivatives of the more effective agents that gave trouble on formation. Since the introduction of a sulfonic acid group into an organic compound ordinarily increases the water solubility and gives a compound which is stable in dilute sulfuric acid, it was logical to study a number of sulfonic acid derivatives.

The results were most interesting. In nearly every instance the presence of a sulfonic acid group resulted in (*a*) a higher N.C. voltage (more nearly that of the control) after the passage of a normal amount of current on formation, and (*b*) a higher initial cold capacity which indicated more normal formation of the active material. The active material appeared to have normal wetting properties when the agent contained sulfonic acid groups.

The position in the molecule occupied by the sulfonic acid group had a definite influence upon the cold rate. Compounds in which the sulfonic acid group was the only substituent were ineffective. The sulfonic acid-containing agents had initial cold capacities at or near their maximum and several of them, upon cycling, dropped below the control level to values indicating a definite detrimental effect.

Nitrogen and sulfur analogs.—The three compounds H_2O, H_2S, and H_3N form three series of derivatives that have many related properties. These compounds may be considered as the replacement of the oxygen in H_2O with sulfur or the —NH— group, or the replacement of the —OH group by —SH or —NH_2. A number of such compounds were tested because of the occurrence of these compounds in natural materials used as expanders.

In general, the oxygen compounds were the better expanders with the nitrogen analogs tending to give lower negative-to-cadmium potentials. A number of xanthates were studied and found to have very little effect on cold capacity although they did raise the final N.C. formation potential toward zero (by about 0.05 volts).

When agents containing nitrogen, either as amines, amides, or nitro groups, were being studied, frequent tests of the electrolyte were made in an effort to detect nitric acid which perhaps could result from electrolytic action. In no instance was it possible to detect the presence of nitric acid even when the agent contained a nitro group.

Effect of addition agents upon plate expansion.—The final apparent thickness of the tested negative plates (after about 70 cycles) compared to the thickness of the control negatives showed that there was no relation between the addition agent effect upon cold capacity and the apparent thickness of the negative plate. Some addition agents that produced the great-

est expansion gave the lowest cold capacities. On the other hand, some effective agents gave less expansion than the control negatives. Plate expansion data, however, are not precise because of their dependency upon the tightness of the assembly of the elements in the cell.

Discussion of Results

In a previous paper (1) a point of view on expander action was developed from a study of the literature of addition agents, which in effect said that the actual beneficial agent was produced *in situ* by the electrolytic action of formation and cycling upon the organic matter added to the negative plate. Proper treatment of the organic matter before adding it to the active material of the plate would greatly increase its initial effect, and perhaps reduce any possible gain in effectiveness with cycling. Regardless of the source or nature of the organic material added to the negative plate the previous paper concluded that, the final material, or the active agent in the plate, appeared to be of such nature to be best described as a "humic substance."

The experimental data reported here lend support to this point of view, although there are yet many unexplained relations. It is recognized that the degradation of carbohydrates and the oxidation of phenols and their homologes yield products characterized as "humic substance." From these two classes of pure compounds came the most effective agents tested in this study.

Compounds with marked reducing properties as the aldehydes, quinones, and some of the aromatic hydroxyl compounds showed beneficial effects initially. The relatively stable carboxyl acids, the alcohols, and the ketones were of little effect either before or after cycling. The aldehydes which are easily reduced to alcohols or oxidized to acids, both of which are of little effect, lost most of their beneficial action with cycling. The carbohydrates, which, although soluble, apparently were only slowly attacked under the conditions of their use in this study, had little initial effect but showed large gains by cycling.

Solubility of the agent, if accompanied by reducing properties, appears to have made for good initial effects. Insoluble agents gave poor initial results because they interfered with the development of the active material, and their low solubility also reduced the rate at which the electrolytic action of the battery might modify the original compound to an effective form. The influence of a solubilizing sulfonic acid group upon an otherwise difficultly soluble compound was to facilitate formation and increase the initial effect, although after cycling the effect may be reduced.

It is logical to believe that the effectiveness of lignin sulfonic acid derivatives, both initially and after cycling, are related to the reducing properties of their phenolic groups, and the solubilizing action of the sulfonic acid group.

Acknowledgment

The author wishes to express his appreciation to the Eagle-Picher Company for permission to publish this study.

Any discussion of this paper will appear in a Discussion Section, to be published in the December 1953 issue of the Journal.

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The Effect of Humidity upon the Insulation Resistance of Alkyd Molding Compounds[1]

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ABSTRACT

There are a large number of plastics available to the electrical engineer for consideration as dielectrics. Current electrical requirements are much more rigorous than those of former years, consequently some of the older, well-established plastics fail to meet them. The property in which there is much interest is the behavior of insulation resistance with variations in humidity.

Among the new plastics being tested for insulation resistance are alkyd molding compounds. These compounds deteriorate slowly under high humidities due to the hydrolysis of the polyester linkages. By judicious choice of acids and glycols in the resin and by careful selection of the fillers used, the effect of humidity is drastically reduced.

INTRODUCTION

This paper presents data on the deterioration of the insulation resistance of new, commercially available, thermoset alkyd plastics after exposure for increasing periods of time to high humidities and temperatures. For purposes of comparison and control, data on well known and commercially accepted phenolic and melamine plastics are included. The plastics chosen for testing were: Resimene 803A; Melmac P592; Durez 12810; Resinox 7934; Bakelite BM64; Plaskon 420; and Plaskon 422.

Resimene 803A is a cellulose-filled melamine formaldehyde molding compound specifically designed for electrical connector inserts.

Melmac P592 is a mineral-filled melamine molding compound recommended for electrical insulation applications.

Durez 12810 is a special grade phenolic molding compound designed for use where good electrical properties are necessary.

Resinox 7934 is a superior grade low-loss phenolic molding compound for electrical usage.

Bakelite BM64 is a general purpose phenol-formaldehyde molding compound.

Plaskon 420 and 422 are alkyd molding compounds designed for industrial and electrical applications.

Pertinent physical properties of these plastics are listed in Table I.

TABLE 1. *Physical properties of plastics tested**

	Resimene 803A	Resinox 7934	Durez 12810	Melmac P592	Bakelite BM64	Plaskon 420	Plaskon 422
Specific gravity	1.45	1.76	1.89	1.70	1.40	2.20	2.20
Water absorption 24 hr, %	0.60	0.03	0.02	0.50	0.55	0.14	0.08
Flexural strength, psi	10,000	9,000	9,500	6,000	10,000	9,000	8,000
Impact strength (Izod)ft lbs/in. of notch	0.32	0.37	0.34	0.32	0.30	0.33	0.33
Heat distortion, °C	149	—	143	—	160	191	191
Arc resistance, sec	125	3	3	133	5	190+	180+
Dielectric constant 10^6 cycles	6.70	4.30	—	5.65	5.4	4.70	4.20
Dissipation factor 10^6 cycles	0.050	0.008	—	0.040	0.04	0.017	0.014
Dielectric strength, short time test per ASTM D-149, volts per mil	400	425	400	535	330	475	420

* Data are an average of published ranges.

TEST METHODS

The effect of temperature and humidity on insulation resistance was determined according to ASTM Specification D257–38. To facilitate the expression of results of these tests, it became necessary to devise a new electrical term "insulation life." The insulation life of a dielectric is the length of time required for the insulation resistance to fall below an arbitrary figure under a given set of ambient conditions. For example, the 1000 megohm insulation life at 74°C and 95 per cent relative humidity would

[1] Manuscript received May 13, 1952. Paper prepared for delivery before the Philadelphia Meeting, May 4 to 8, 1952.

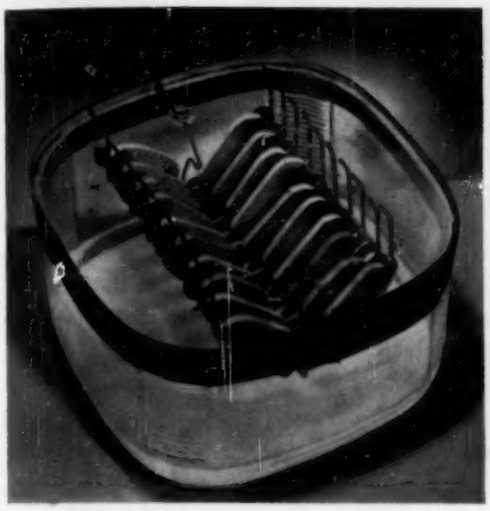

FIG. 1. Special humidity testing jar

TABLE II. *Insulation life of commercial polyesters*

Name of polyester	Catalyst concentration, %	100,000Ω insulation life, days
Plaskon 911-11	2	45
Plaskon 947 laminating resin	2	53
Selectron 5003	2	49
Paraplex AP43	2	31
Laminac 4128	2	70
Laminac 4126	2	105
Interchemical 86	2	45
Plaskon 947 laminating resin	0.1	48
Selectron 5003	0.1	48
Paraplex AP43	0.1	48
Laminac 4128	0.1	35
Laminac 4126	0.1	105

TABLE III. *Insulation resistance in megohms at 38°C and 95% relative humidity*

Type of material	20 Days	60 Days	80 Days	100 Days
422	1800	400	260	230
803A	400	140	120	110
P592	1000	75	41	14
7934	180	33	19	12
BM64	1.9	—	—	—

TABLE IV. *Insulation resistance in megohms at 71°C and 95% relative humidity*

Type of material	2 Days	6 Days	12 Days	16 Days
422	5000	2500	1600	1200
12810	380	190	120	105
803A	300	160	110	100
P592	1000	25	2.5	1.5
420	60	2	—	—

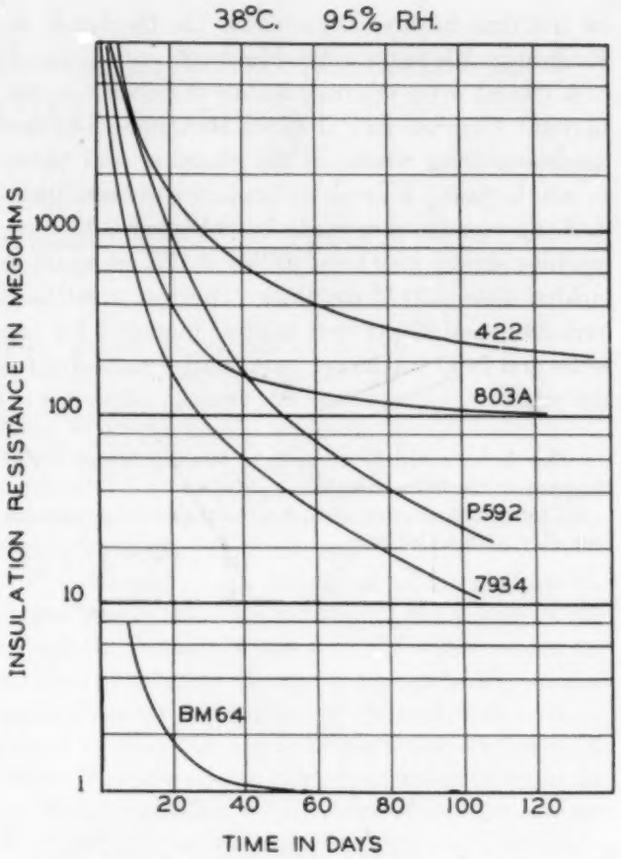

FIG. 2. Insulation resistance at 38°C and 95 per cent relative humidity.

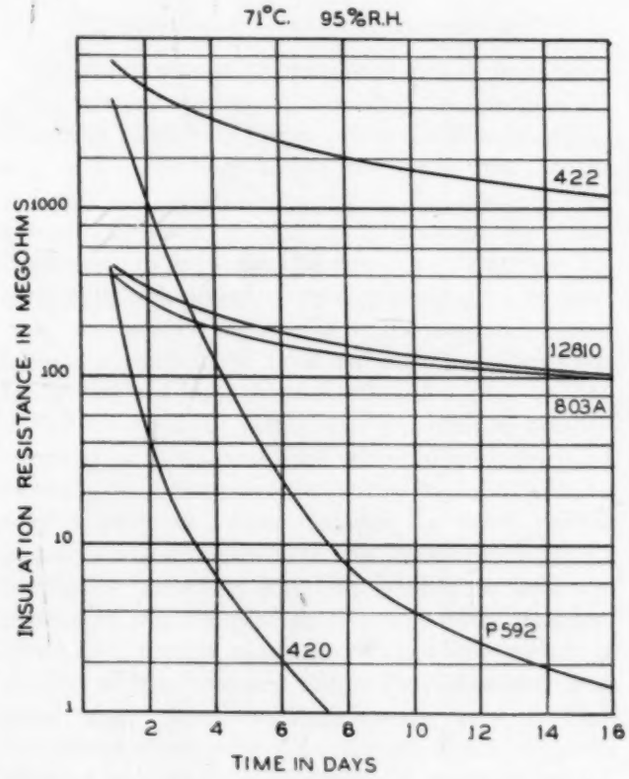

FIG. 3. Insulation resistance at 71°C and 95 per cent relative humidity.

be the time in days required for the insulation resistance to fall below 1000 megohms.

A special oven or conditioning chamber was employed.[2] Covered jars (Fig. 1) containing the test specimens were placed in the chamber and tested *in situ* by using a probe to contact each test specimen. Specimens were made by inserting 0.3175 cm machine screws into holes drilled 3.175 cm apart in molded disks 0.3175 cm thick. The test conditions were 38°C and 95 per cent relative humidity for one series and 74°C and 95 per cent relative humidity for the other.[3]

[2] The authors will be pleased to forward blueprints of the oven to those interested.

[3] A saturated solution of K_2SO_4 maintained the requisite humidity within the jars.

Conclusions

The insulation life of unfilled polyester resins is satisfactory for most dielectric needs (Table II). When any of these resins are compounded with fillers and other components to make molding compounds, the insulation life deteriorates rapidly at high humidities and temperatures. By carefully controlling the type of filler and surface treatments thereof, concentration ratios of alkyd component and modifying monomers, type and concentration of catalysts and methods of processing, molding compounds result which have a good insulation life. Data are listed in Tables III and IV and are plotted as graphs in Fig. 2 and 3.

Any discussion of this paper will appear in a Discussion Section, to be published in the December 1953 issue of the Journal.

The Testing of Magneto Insulation for Arc Resistance and Resistance to Spark Atmospheres[1]

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ABSTRACT

Experience gained in the production of ignition equipment, electrical connectors, and associated items indicates that certain tests are significant in predicting the performance of dielectric parts. It is our intention to discuss the methods and equipment used to conduct these tests and the interpretation of the results.

Introduction

Aircraft ignition equipment necessitates the harnessing of high voltages in the smallest possible space under operating conditions present at altitudes up to 65,000 ft. Under these conditions two factors have been found to be of more importance in the selection of insulating materials than would normally be the case. These are arc resistance and the resistance of the material to spark atmospheres.

Magneto Arc Resistance

In this laboratory, materials which are being considered for magneto or other ignition applications are tested under a spark gap similar to that used in the original A.S.T.M. method (1), but fired by a high tension magneto. The magneto arc consists of a series of sparks, each differing in polarity from the one preceding. The frequency of sparking is regulated by the speed at which the magneto is operated. Only at the higher speeds does this series of sparks develop the characteristics of a true arc or ionized gap. At the lower spark frequencies each spark is very distinct from those immediately preceding and following it, and the test is very sensitive in eliminating those materials which Olyphant (2) has described as "tracking sensitive" and which normally carbon-track under the first few sparks. The materials which are not tracking sensitive do not carbon-track at the low frequencies although tests have been extended for several hours. At the higher spark frequencies, the test tends to separate "tracking insensitive" materials into classes more or less the same as the A.S.T.M. procedures (1, 3).

Effects on arc resistance of the decreased air pressures.—These effects are presented in Fig. 1 for four materials extensively used as magneto insulation. Tests were conducted under a bell jar at air pressures simulating those present at the altitudes under consideration. The conical, pointed electrodes, having a one-half inch spacing, were fired by a magneto producing 3000 sparks per minute.

The increase in arc resistance as the altitude increases lies in the visible lifting of the center of the arc off the surface of the material. This occurs regardless of whether the arc is placed in the normal position on the top surface of the specimen or is reversed so that the arc is beneath the specimen. It results from the release of gaseous materials from the specimen, instituted by the heat of the arc and accelerated by the low ambient pressure. The results indicate that arc resistance at higher altitudes cannot be predicted from values obtained at sea level.

Resistance to Spark Atmospheres

Resistance to spark atmospheres is a term applied to the relative resistance a material offers to chemical attack by nitric acid fumes which result from oxidation of the nitrogen in the air in the presence of moisture and which are caused by arc discharges in a confined space. Attack on a material by these fumes results in a marked decrease in surface resistivity which promotes surface creepage with possible permanent failure by carbonization. Many failures attributed to poor arc resistance have actually resulted from this condition.

The most serious attack found in this laboratory occurred on a mineral-filled material and consisted basically of a conversion of water-insoluble salts to soluble nitrates. This material, a hard rubber magneto insulation which had excellent electrical properties including humidity resistance and arc resistance, was occasionally found to suffer considerable loss in insulation resistance after long periods of service, with subsequent failure by carbonization in some cases. Accelerated endurance tests at high humidities duplicated this, the hard rubber parts showing the presence of beads of moisture on all surfaces, particularly on machined surfaces, resulting in extremely low surface resistance.

[1] Manuscript received May 6, 1952. This paper was prepared for delivery before the Philadelphia Meeting, May 4 to 8, 1952.

The filler of this material consisted primarily of calcium carbonate and iron oxide, the former being soluble in nitric acid. An analysis of the moisture

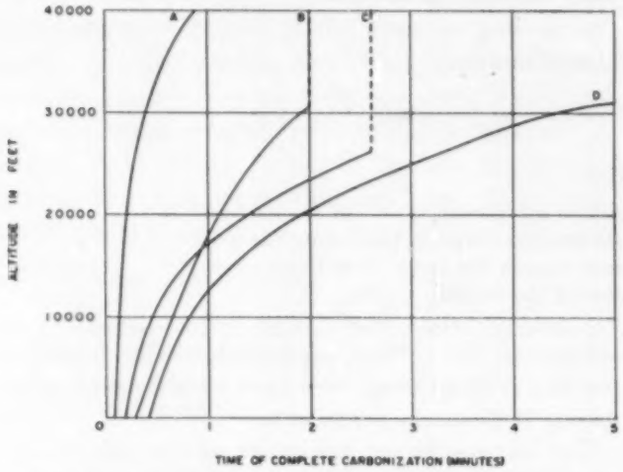

FIG. 1. Illustration of the effect of low ambient pressures on arc resistance of various dielectric materials. A—Hard natural rubber; B—Buna N hard rubber; C—Buna S hard rubber; D—Mineral filled melamine.

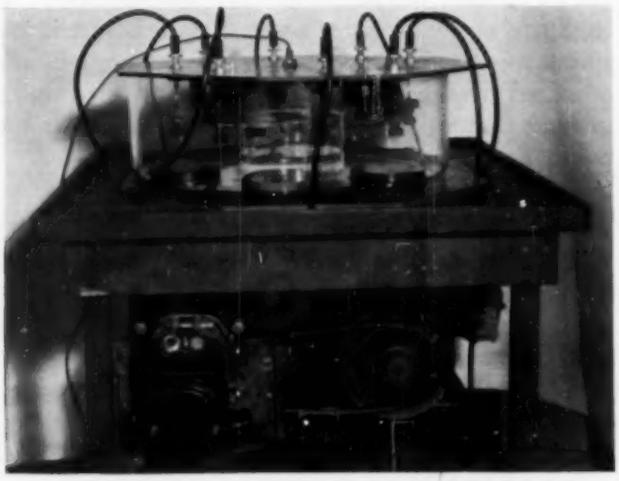

FIG. 2. Equipment used to evaluate the resistance to spark atmospheres offered by various dielectric materials.

beads showed them to contain calcium nitrate. To prove our theory an experimental compound was produced in which the calcium carbonate was replaced by additional iron oxide. This material showed none of the effects previously encountered.

In some infrequent cases the resin itself is affected and although the processes are apparently more closely allied with accelerated oxidation and sometimes hydrolysis, the end effects are very similar. Most materials show little more effect than under extremely high humidity, but those which are attacked by the fumes are much more seriously and permanently affected than by humidity alone.

The test equipment employed is shown in Fig. 2 and consists simply of a closed glass chamber having a laminated phenolic cover on which are mounted eight spark gaps fired by a motor driven magneto located outside the chamber. A beaker of water is placed in the chamber to maintain high humidity. The size of the chamber, number of gaps, and source of energy can be varied according to the equipment available as this test can, at present, only be conducted on a comparative basis. Results are normally indicative at the end of 24 hours, and the effects can be determined by use of standard insulation resistance measuring equipment. It is advisable to test a known good material and a known poor material as standards with the unknown material.

The above tests are primarily intended for the evaluation of materials to determine their acceptability as ignition insulation. They cover specific characteristics of vital importance which may not be found by conventional tests. They have the advantage of closely duplicating conditions present in service, thereby eliminating the necessity of attempting to predict service performance from standard tests which for reasons of expediency may vary considerably from actual operating conditions.

Any discussion of this paper will appear in a Discussion Section, to be published in the December 1953 issue of the JOURNAL.

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Streaming Potential Measurements and the Adhesion of Phosphors on Cathode Ray Screens[1]

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ABSTRACT

Streaming potential measurements were carried out to determine the effect of barium acetate on the zeta potentials of phosphor and glass surfaces in the presence of potassium silicate. The results are compared with previous data for sodium sulfate as the addition agent. Although widely different concentrations of the two salts were required to depress the zeta potentials to the same low values, the concentrations corresponded to those which give good adhesion of phosphor to glass. The mechanism of adhesion is discussed.

Introduction

Previous reports from this laboratory on streaming potential measurements with phosphors (1) and on the adhesion of phosphors on cathode ray screens (2) have dealt with the role of sodium sulfate as an addition agent to potassium silicate.

The present study was designed to clarify the role of barium acetate which may be substituted for sodium sulfate as addition agent. It is known that the concentration of barium salt required to produce adhesion is much lower than of sodium sulfate.

Experimental Procedure

Materials

Phosphors: Du Pont No. 1630 phosphor, zinc sulfide-zinc cadmium sulfide; R.C.A. No. 33-Z-8 phosphor, zinc beryllium silicate.

Glass

Corning No. 774 glass (crushed Pyrex—150 mesh); Corning No. 9010 glass (crushed to pass a 100 mesh screen).

Sodium sulfate, barium acetate, and potassium chloride: analytical reagent grade.

Potassium silicate: Kasil No. 1, Philadelphia Quartz Company (analysis: 7.8% K_2O, 19.5% SiO_2; sp gr 1.25; molecular ratio, K_2O: 3.92 SiO_2). Stock solutions of the silicate were prepared fresh daily.

Apparatus

The apparatus employed is shown in Fig. 1 and is a modification of the one described previously (1). Improvements were as follows. The glass tubing from the streaming cell to the calomel half-cells had an outside diameter of 10 mm instead of 4 mm. This reduced the resistance between the half-cells to a marked extent[2] and made possible the use of switches in the circuit. The comparatively low resistance of the circuit also made it possible to use a potentiometer and galvanometer for measurements of the potential even in the case of dilute solutions. All electrical connections were made with test prod wire (Belden No. 8899) and the connections near the apparatus were enclosed in rubber tubing to prevent electrical leakage.

Measurements

The powders under investigation were confined between perforated platinum electrodes using a section of rubber tubing as the cell compartment (1). The diaphragm assembly is shown in Fig. 2. Silver-silver chloride electrodes having the same shape as the platinum electrodes were substituted for the latter in a number of experiments. Since these electrodes were not polarized, they were used for potential determinations as well as for conductance measurements.

In general, the zeta potentials determined with the silver-silver chloride electrodes corresponded with those using calomel electrodes. In runs with 0.0100*N* potassium chloride and with Kasil No. 1 solutions of concentrations from 0.05 per cent to 20 per cent, zeta potentials measured alternately with the calomel and with the Ag-AgCl electrodes agreed to 1 mv. At higher concentrations the calomel electrodes appeared to have greater stability. Other investigators (3) have found Ag-AgCl electrodes to be somewhat polarized at high solution concentrations especially in the absence of chlorides.

In several series of experiments the powders were contained between platinized platinum electrodes

[1] Manuscript received June 4, 1952. This paper was prepared for delivery before the Philadelphia Meeting, May 4 to 8, 1952.

[2] With 0.010*N* potassium chloride solution the resistance was about 40,000 ohms instead of the previous 300,000 ohms.

which were employed for both potential and resistance measurements. The platinized electrodes gave reproducible potential measurements and because of their great insolubility and extensive surface area were preferred to the Ag-AgCl electrodes.

No two electrodes, whatever the type, were found to have the same potential values. Potential measurements were taken, accordingly, with no flow in order to obtain a zero correction value. The potential correction remained quite constant for a given pair of calomel electrodes but the corrections tended to change slowly with time for both Ag-AgCl electrodes and platinized platinum electrodes. The two features, constancy of potential and complete reversibility, give calomel electrodes an advantage for potential measurements in the present system.

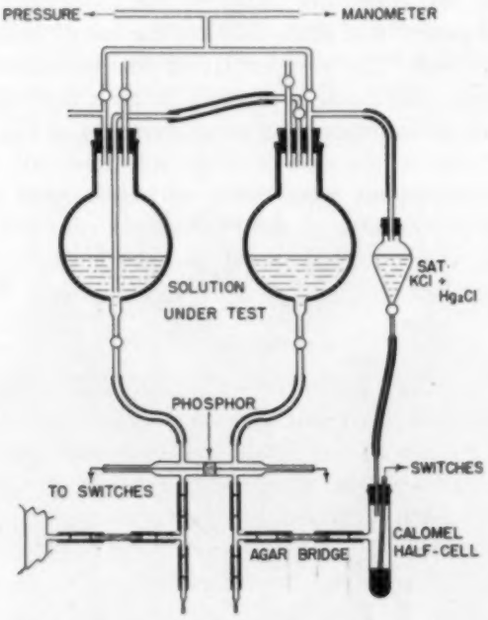


FIG. 1. Streaming potential apparatus

In the determination of streaming potentials, the solution under test was permitted to stream through the diaphragm for 15 minutes[3] at a hydrostatic pressure of 40 cm of Hg before the first potential reading was made. Four readings were taken at five-minute intervals at this pressure for each solution employed. Zero-pressure potential readings were taken before and after each streaming potential measurement, averaged, and applied as a correction to the streaming potential. Despite the fact that the correction factors varied widely for each of the electrode pairs, when these corrections were applied to the measured streaming potentials, the corrected values for the different electrode pairs were in good agreement. Illustrations are given below. Two different calomel electrode pairs are used in the illustrations.

Electrode pair	Measured streaming potential (40 cm pressure)	Potential correction (no pressure)	Corrected streaming potential
Calomel	−9.3 mv	+2.9 mv	−12.2 mv
Ag-AgCl	−13.6 mv	−1.3 mv	−12.3 mv
Calomel	−15.5 mv	−5.5 mv	−10.0 mv
Platinized Pt	−7.7 mv	+2.3 mv	−10.0 mv

The cell constants for the packed diaphragms were obtained using 0.100*N* KCl.[4] The resistance measurements necessary for the calculation were made during streaming. This procedure was decided upon when it was discovered that, with no flow, the conductance of dilute solutions in cells filled with powdered glass increased sharply with time due to solubility of the glass. The cell constant was determined before and after each series of streaming potential measurements. The two values of the cell constant, which never differed by over a few per cent, were averaged for the purpose of calculating the zeta potential.

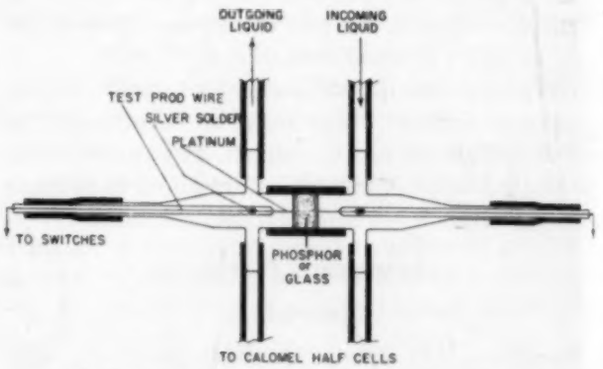


FIG. 2. Streaming potential diaphragm assembly

RESULTS

The data are presented graphically in the accompanying figures in plots of zeta potentials against concentration of potassium silicate or of added salt. The zeta potentials were calculated from a knowledge of the streaming potential, cell constant, cell resistance, and pressure difference by the method described previously (1).

[3] Conductance data indicate that this time is more than adequate to displace the previous solution from the streaming cell.

[4] Cell constants for diaphragms filled with phosphor and with powdered glass were determined using 0.0100, 0.100, and 1.00*N* KCl and with saturated sodium chloride solution. All solutions gave the same cell constant indicating negligible surface conductance. This was not the case with more dilute solutions where appreciable surface conductance was encountered.

Effect of Potassium Silicate on the Zeta Potentials of Phosphors and Glasses

The effects of potassium silicate concentration[5] on the zeta potentials of R.C.A. No. 33-Z-8 phosphor and Du Pont No. 1630 phosphor are shown in Fig. 3. The general shape of the curves is the same and strong negative potentials are produced with both phosphors, indicating adsorption of silicate on the solid surfaces. A falling off of negative potential with

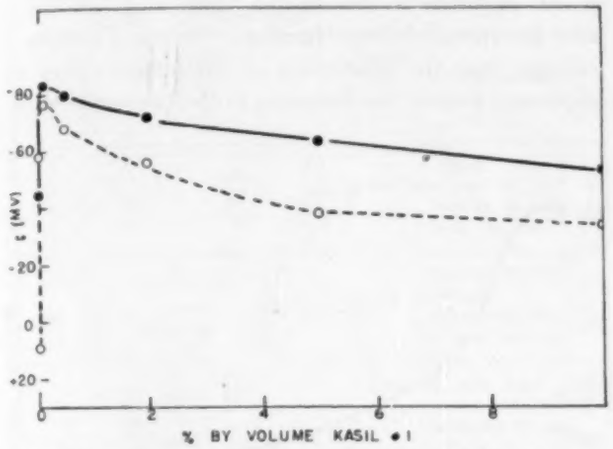


FIG. 3. Results with different phosphors. ● R.C.A. No. 33-Z-8 phosphor; ○ Du Pont No. 1630 phosphor.

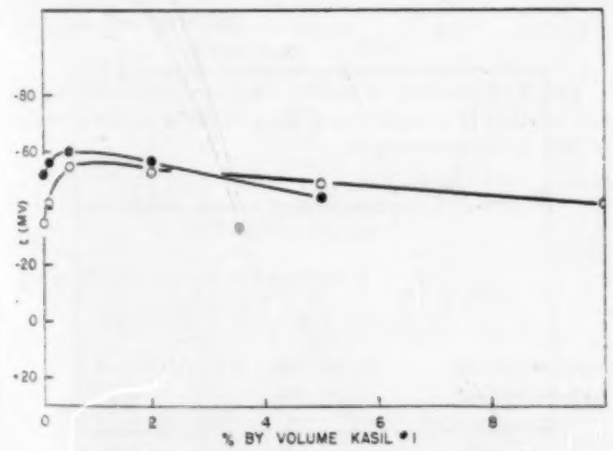


FIG. 4. Results with different glasses. ● Corning No. 774 (Pyrex) glass; ○ Corning No. 9010 glass.

increasing concentrations of silicate occurred after the initial charging. A rather unexpected result was that the Du Pont No. 1630 phosphor had a positive charge in the absence of potassium silicate. This may have been due to flux or other impurity present in it. The addition of the first small increment of potassium silicate recharged the phosphor with a negative sign.

[5] Potassium silicate concentrations are expressed in percentage by volume Kasil No. 1. Since Kasil No. 1 contains 3.41×10^5 ppm of solid K_2O:3.92 SiO_2, a 1 per cent solution contains 3.41×10^3 ppm of this potassium silicate.

Considering that different samples were used, the present results with the R.C.A. No. 33-Z-8 phosphor and potassium silicate agree substantially with those obtained by Edelberg and Hazel (1), except for the point corresponding to the highest concentration of silicate. These investigators found no drop in negative potential despite the fact that a fall in negative potential was suggested by the point corresponding to 1.2 per cent silicate. It is thought that the discrepancy is due in part, at least, to the fact that a new cell was employed by the previous workers for the measurement at the highest concentration. It has since been found that such cells give higher negative potentials than those which have been in use.

The negative potential of glass surfaces also was increased strongly at low concentrations of added silicate. This is shown by the data in Fig. 4 for

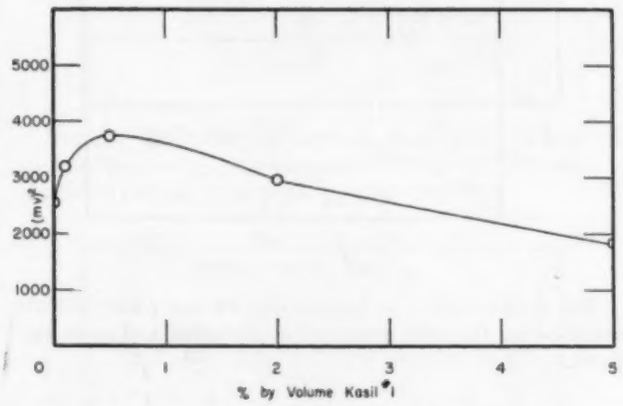


FIG. 5. Effect of potassium silicate on the zeta potential product of Corning No. 9010 glass and Du Pont No. 1630 phosphor.

Corning No. 774 glass (Pyrex) and Corning No. 9010 glass.

Since the negative potentials of both phosphor and glass surfaces are increased in dilute solutions of silicate, the mutual repulsion between the surfaces increases under those conditions. The repulsion between the surfaces may be expressed in terms of the zeta potential of the glass surface multiplied by the zeta potential of the phosphor surface for different silicate concentrations. This plot is given in Fig. 5 for Corning No. 9010 glass and Du Pont No. 1630 phosphor.

Effect of Mixtures of Potassium Silicate and Salts on the Zeta Potentials of Phosphors and Glasses

The effect of mixtures of potassium silicate and barium acetate upon the zeta potentials of the surfaces is shown in Fig. 6. The potassium silicate was maintained at a constant value of 2040 ppm and the concentration of barium acetate varied. Du Pont No.

1630 phosphor and Corning No. 9010 glass powder were employed as the solid surfaces.

These data represent the average of several runs. Zeta potentials for both glass and the phosphor were found to be negative in all cases, but are plotted in opposite directions from a zero ordinate in order to show the relative repulsion under varying conditions (1). The effect of barium acetate in decreasing the

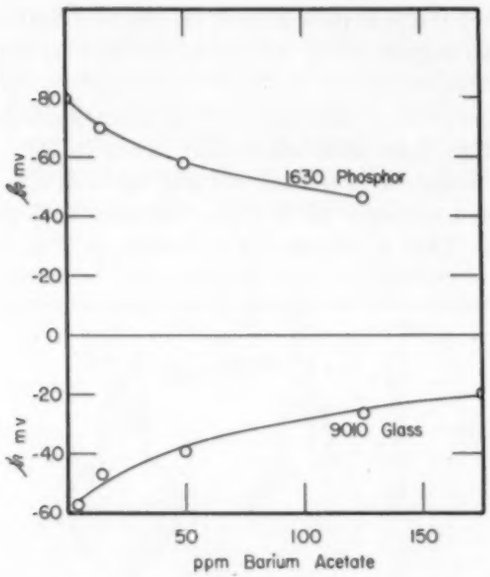


FIG. 6. The effect of barium acetate-potassium silicate mixtures on the zeta potential of phosphor and glass surfaces.

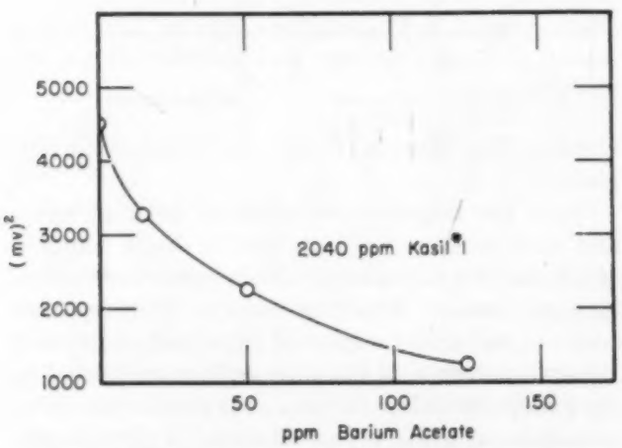


FIG. 7. The effect of barium acetate on the zeta potential product of phosphor and glass surfaces in the presence of 2040 ppm potassium silicate.

repulsion between the two surfaces under these conditions is shown also in Fig. 7, in which the product of multiplying the zeta potential of the phosphor surface times the zeta potential of the glass surface is plotted against the barium acetate concentration.

Similar results to those shown in Fig. 6 were obtained by Edelberg and Hazel on R.C.A. No. 33-Z-8 phosphor and Pyrex glass wool with potassium silicate-sodium sulfate mixtures (1). The effect of sodium sulfate in decreasing the repulsion between these two surfaces in the presence of 3600 ppm of potassium silicate is shown in Fig. 8. A comparison of Fig. 7 and 8 shows that the concentrations of these two salts required to produce a lowering of the zeta potential product to an arbitrary value of 1000 are markedly different. These concentrations are of the same order of magnitude as will give good screens, however. The data in Table I, showing the amount of salt required to reduce the value of $\zeta\zeta'$ to 1000, were interpolated from the above figures. These data indicate that the potentials of the surfaces play an important role in the adhesion in the present system.

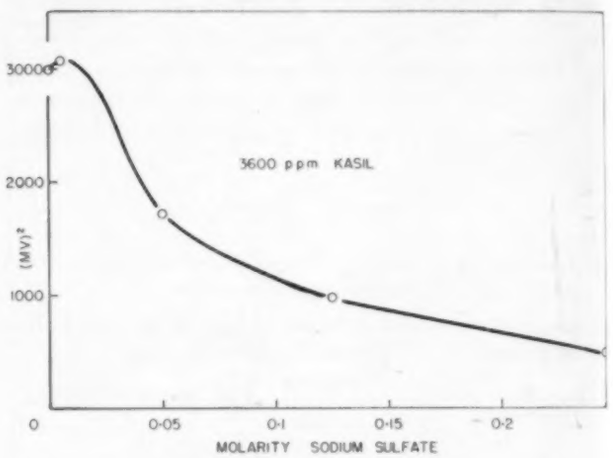


FIG. 8. The effect of sodium sulfate on the zeta potential product of phosphor and glass surfaces in the presence of 3600 ppm potassium silicate.

TABLE I. *Comparison of sodium sulfate and barium acetate*

Salt	Conc of salt required to reduce $\zeta\zeta'$ to 1000	
	Ppm	Molarity
Barium acetate	100–200	3.7×10^{-4}–7.3×10^{-4}
Sodium sulfate	14,200	0.1

As expected from electrokinetic behavior the valence of the positive ion determines the concentration of salt required to reduce the potential to a given low value. The choice of cation is limited by the *p*H of the silicate system. Metals whose hydroxides precipitate at *p*H values below about 10 are eliminated from consideration; hence tri- and tetravalent cations cannot be employed. Indeed, only ions of the strongly basic metals, the alkalies and alkaline earths, are stable in solution at this *p*H.

The Adhesion of Phosphors

The effects of potassium silicate and of potassium silicate-salt mixtures in promoting adhesion of phosphor to glass may be discussed with the aid of the

diagram in Fig. 9. The dotted line running from top to bottom divides the electric double layers of the solid phosphor surface (shaded area to the right) and of the solid glass surface, represented by the shaded area to the left. The surfaces are negatively charged and are kept apart by electrical repulsion. The repulsion is weak in the presence of water (indeed with the No. 1630 phosphor, which is positive in water, a weak attraction would appear to be possible, although adhesion is weak in the absence of silicate).

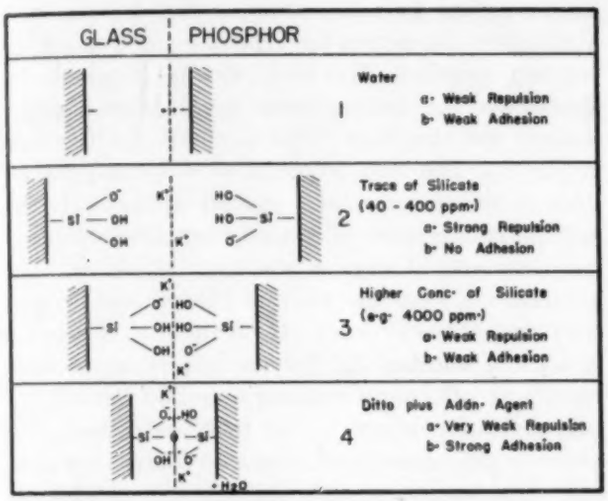


FIG. 9. Diagrammatic illustration of the effect of potassium silicate and addition agents on the bonding of glass and phosphor surfaces.

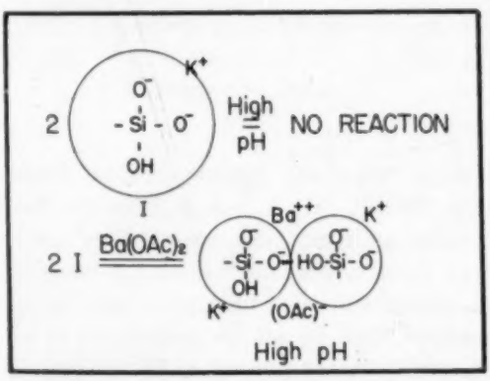


FIG. 10. Diagrammatic illustration of the effect of barium acetate on polymerization at high *p*H.

The addition of a trace of silicate increases the repulsion between the surfaces by increasing the negative potentials (cf. Fig. 5). At higher silicate concentrations the surfaces become saturated with silicate. The double layer is less diffuse, i.e., is thinner, under these conditions because the potassium silicate in solution tends to screen the charges in the electric double layer of the adsorbed silicate. This condition corresponds to the falling off of zeta potential at high silicate concentrations. The repulsion between the surfaces keeps them too far apart for the adsorbed silicate to polymerize, however. Not until a salt is added (condition 4 of Fig. 9) and the surface charges are more effectively screened does polymerization of the adsorbed silicate occur. The polymerization takes place preferentially at the solid surface rather than in the bulk of the solution because the silicate is concentrated by adsorption at the solid interfaces.

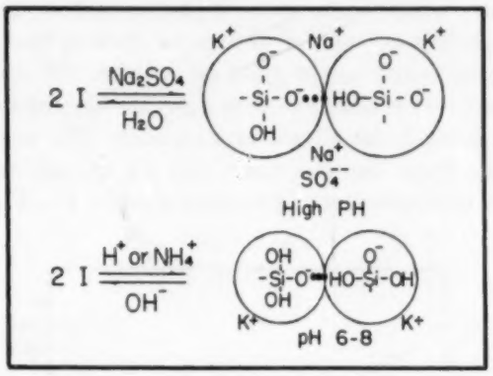


FIG. 11. Top: diagrammatic illustration of the effect of sodium sulfate on polymerization. Bottom: illustration of the effect of reduction of *p*H on polymerization.

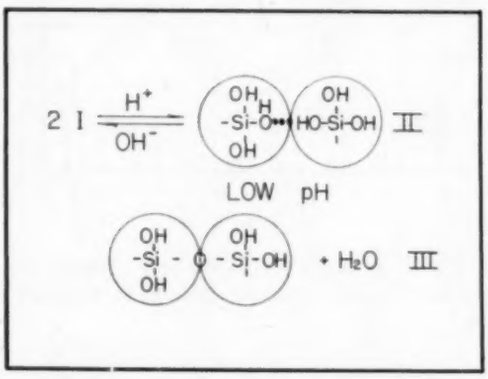


FIG. 12. Illustration of the types of bonds that may hold the polymer together at low *p*H.

Polymerization of Silicates

The polymerization of silicates can be discussed with the aid of Fig. 10–13. At high *p*H values the number of charges per silicate ion is high. The ions repel each other and the polymerization reaction is prevented. The charges can be screened by the addition of salts which crowd in the double layer and reduce the repulsion between the ions. Polymerization of the silicate then occurs. In Fig. 10 and 11 the thickness of the double layer is indicated by the diameter of the circle surrounding the silicate ion. The double layer of the silicate ion at high *p*H, structure I, is pictured being compressed by barium acetate, Fig. 10, and by sodium sulfate, Fig. 11. As indicated in Table I, a much lower concentration of

barium salt than sodium salt is required for polymerization.

The bonds holding the silicate ions together in the polymer, or gel, at high *p*H are weak. A revealing experiment can be carried out as follows. Mix equal 25 ml portions of Kasil No. 1 and 4*N* sodium nitrate in a small beaker. A stiff gel which can be retained in an inverted beaker will form within 2 to 3 minutes. If now the gel is transferred to a beaker containing 500 ml of distilled water and stirred, it will dissolve within 5 minutes. The bonds that are present in this salt-gel are of the same nature that hold phosphor particles to glass on cathode ray screens. When water is added to such a gel, the electric double layer around the silicate ions expands. The negative charges force the ions apart and the silicate returns to the monomeric structure indicated by I in Fig. 10.

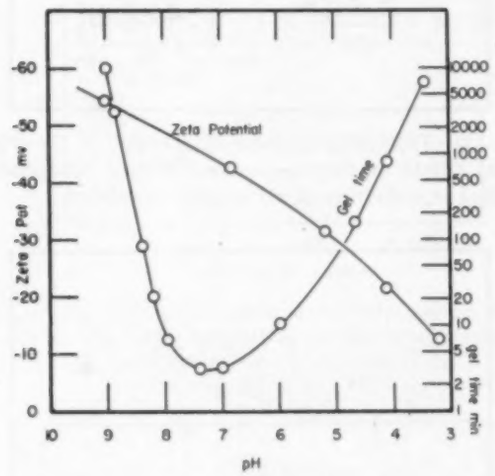
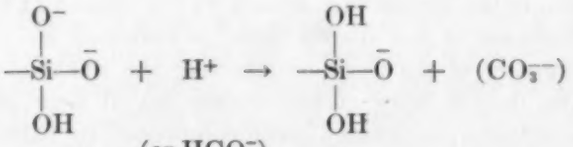


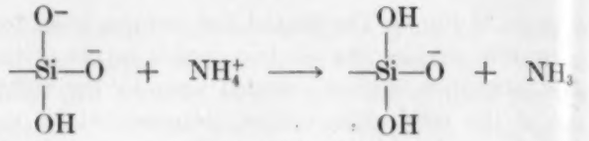
FIG. 13. Effect of *p*H on the gel time (Merrill and Spencer) and on the zeta potential (Hazel) in aqueous silicate systems.

*Polymerization by Reduction of p*H

Silica gels or silicate polymers may be formed by reduction in *p*H. This may be accomplished by the addition of acids, ammonium salts, or acid salts (e.g., $NaHCO_3$ or $KHSO_4$) to silicates. The electric charges on the silicate ions are neutralized. Water will not effectively dissolve gels formed by lowering the *p*H because there are not enough negative charges in the polymer to break it up into small fragments. The reaction involved in neutralizing the charges is indicated below.



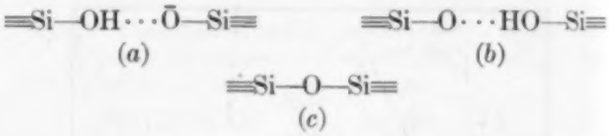
Acid or acid salt



Ammonium salt

The polymerization which occurs following the reduction in *p*H and charge is illustrated in the lower half of Fig. 11 and in Fig. 12.

Too great a reduction in charge is not desirable for maximum polymerization, a fact replete with implication concerning the type of bonds holding the polymer together. The best evidence available indicates that maximum gelation occurs when negative charges are abundant. This is shown by the data in Fig. 13. The zeta potential of silica and the gel time of silicates are both plotted against *p*H. The zeta potentials were calculated from electrophoresis measurements of silica sols at varying *p*H (4). The gel data are from the work of Merrill and Spencer who studied the effect of *p*H on the rate of gelation of sodium silicates (5). Polymerization occurs most rapidly at *p*H values between 6 and 8.[6] Since faster polymerization occurs under these conditions than at lower *p*H where fewer negative charges are present, it is suggested that the negative charges are involved in bond formation. This is indicated by the hydrogen bond designated (*a*) below. Other possible bonds are shown in the text and also in Fig. 12.



Although television screens can be formed by lowering the *p*H of alkaline silicates to the range where rapid gel formation occurs, they are usually produced using a salt which does not lower the *p*H, such as sodium sulfate or barium acetate (or nitrate). This assures that an ample proportion of charged groups, ≡Si—Ō, are present in the system.

[6] Potassium silicate shows a similar gel time-*p*H relationship with maximum gelation occurring in the same *p*H range. A simple experiment which will illustrate this relationship is as follows. Measure 60 ml volumes of 30 per cent Kasil No. 1 (prepared by diluting 30 ml of Kasil No. 1 to 100 ml with distilled water) into each of four 250 ml beakers. Add about 1 ml of Gramercy Universal indicator (Fisher Scientific Co.) to each. Prepare a 1.5 per cent H_2SO_4 solution by volume (15 ml of concentrated acid diluted to one liter with water). For different *p*H values, add acid as indicated below to the silicate in the beakers.

*p*H	ml 1.5% H_2SO_4
10	35
8	55.5
6	62.5
3	65

Acknowledgment

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Any discussion of this paper will appear in a Discussion Section, to be published in the December 1953 issue of the Journal.

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On the Nature of Fluorescent Centers and Traps in Zinc Sulfide[1]

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ABSTRACT

The impurity levels in the energy diagram of a zinc sulfide phosphor are considered to be localized S^{2-} levels lifted above the filled S^{2-} band due to the presence of monovalent positive or trivalent negative activator ions in the lattice. Electron traps are formed similarly by the substitution of S ions by monovalent negative ions or of Zn^{2+} ions by trivalent positive ions. The energy produced when electrons recombine with trapped holes or when holes recombine with trapped electrons is either emitted directly as light or is first transferred to impurity ions. The elements of the iron group give rise to electron traps. The killing action of these elements is explained by assuming that the energy liberated by recombination between holes and electrons in these traps is transferred to the killer ions. The excited ions return to the ground state radiationless because of the presence of many electronic levels between the excited and the ground state. The effect of heat and infrared radiation on the luminescence is discussed. It is shown that, in a phosphor, energy may be transferred by electrons through the conduction band or by holes through the occupied S^{2-} band.

INTRODUCTION

There are several reasons why it seems justified to treat the impurity-activated zinc sulfide phosphors as a separate class. In many respects their properties differ from other impurity-activated phosphors such as silicates, or phosphates activated with cerium, thallium, manganese, rare earth elements, etc. In these phosphors most properties, such as spectral distribution, temperature dependence, and decay of the luminescence, etc., are determined primarily by the activator, and the basic lattice acts only as a modifying factor. In cerium-activated phosphors, for example, the emission always shows a double peak at low temperatures due to electronic transitions of the excited Ce^{3+} ion to the doublet ground state. For thallium-activated potassium chloride the shape and peak of the absorption spectrum have been calculated successfully by assuming that it is the transition from the $^1S_0$ ground state to the $^3P_1$ state of the Tl^+ ion (1). In the sulfide phosphors, however, the emission characteristics seem to be more a property of the lattice itself than of the activator.

Let us consider, for instance, the fluorescence produced by the incorporation of the elements silver, copper, gold, and "zinc." The emission bands all have nearly the same shape and width and the peaks of the bands fall in a fairly narrow range from about 4300 to 5200 Å. These peaks are all shifted to longer wavelengths by the gradual substitution of cadmium for zinc. The magnitude of the shift corresponds to a decrease of energy of about $1.9.10^{-2}$ ev/mole per cent CdS (2). The lon-gwave edge of the absorption spectrum of the pure sulfide is shifted by about the same amount (3).

In other respects, too, the zinc sulfide phosphors deserve to be treated as a separate class. For example, among the elements which have been recognized as activators are lithium (4), sodium (4), indium (5), scandium (5), and phosphorus (6) which are not known as activators in other materials.

Electron traps are formed by the incorporation of a number of elements (7), some of which also act as activators. The depths of most of these traps vary in a regular manner when zinc is substituted by cadmium. In this respect the behavior of traps is very similar to that of the luminescent centers.

In discussing the properties of the zinc sulfide phosphors the well known energy diagram given in Fig. 1 is generally used. Between the uppermost occupied or S^{2-} band and the next unoccupied or Zn^+ band there are localized levels. The levels C near the full band which are normally occupied by electrons are usually attributed to luminescent centers while the levels T, which are normally empty, are responsible for the trapping of electrons. Excitation of the phosphor with 3650 Å radiation then lifts an electron from the occupied level C into the conduction band. These electrons, moving freely through the lattice, may be captured by empty T-levels or they may recombine with empty C-levels under emission of light. The C-levels are associated with the presence of activators and have, therefore, often been considered as ground states of these activators. Luminescence then is a

[1] Manuscript received May 21, 1952. Invited Keynote Address given before the Symposium on Luminescence at the Philadelphia Meeting, May 5, 1952.

direct property of the activator. On the other hand the author (37) has suggested that *C* levels may also arise from S^{2-} ions disturbed by adjacent activator ions. This theory of indirect activation has already been applied by Kröger (4, 5, 43) in discussing the properties of many zinc sulfide phosphors.

After a short review of the theory of indirect activation, the various activators in zinc sulfide phosphors will be discussed to see which of them may belong to this class of indirect activation. It will furthermore be argued that most of the *T*-levels in zinc sulfide phosphors likewise do not belong to impurity elements but to disturbed lattice elements.

Nature of Fluorescent Centers

Kröger and co-authors (5, 8) have shown that the formation of luminescent centers in zinc sulfide activated with Ag, Cu, Au, Zn, Li, or Na is governed by the principle of charge compensation. These elements can be incorporated much more easily if coactivators are also present. The coactivators can be negative ions such as Cl^- or Br^-. But they can also be trivalent positive ions such as Al^{3+}, Sc^{3+}. These facts show not only that the above mentioned activators are present as monovalent ions but also that these ions occupy lattice sites. If the activators were divalent positive ions on lattice sites, or atoms occupying interlattice sites, no coactivators would be necessary for their incorporation. If they were ions occupying interlattice positions, the fact that both negative ions and positive ions can be used as coactivators would be difficult to explain. But if a divalent Zn^{2+} ion is replaced by a monovalent positive activator ion, the missing positive charge is compensated for either by replacing a divalent negative S^{2-} ion by a monovalent halogen ion, or by replacing a second Zn^{2+} ion by a trivalent positive ion.

It is unlikely that these monovalent activator ions are further dissociated by the exciting radiations or that they are even excited. This holds especially for the alkali ions. For the free Li^+ ion the distance between ground state and the first excited state is 59 ev and its dissociation energy is 75 ev. It is hard to believe that incorporation in the zinc sulfide lattice would lower these energies to such an extent for ionization or excitation to become possible by the absorption of light quanta of only a few electron volts.

Absorption in a pure zinc sulfide crystal of radiation with a wavelength shorter than the edge of the fundamental absorption brings an electron from a S^{2-} ion to a state in which it can move freely through the lattice. One might therefore say that excitation with such radiation leads to ionization of the S^{2-} ions. One of the factors which determines the magnitude of the dissociation energy is the Madelung potential of the S^{2-} ion (9, 10). A lack of positive charge in the immediate vicinity of an S^{2-} ion, such as is created by the replacement of one of the neighboring Zn^{2+} ions by a monovalent positive ion, must raise the Madelung potential of this S^{2-} ion, and thus lower its dissociation energy. An accurate estimation of the decrease in dissociation energy is difficult to make since the lattice will try to compensate for the lack of charge as much as possible by a displacement and polarization of the ions surrounding the monovalent activator ion, but it may well be of the order of 0.5 — 1 ev.

The new absorption band appearing on the long-wave side of the edge of the fundamental absorption when zinc sulfide is activated with copper (8, 11), for example, is thereby explained. Excitation in this new absorption band, known to produce photoconductivity, may then be written as:

$$(S^{2-}A^+) + h\nu \rightarrow (S^-A^+) + \oplus$$

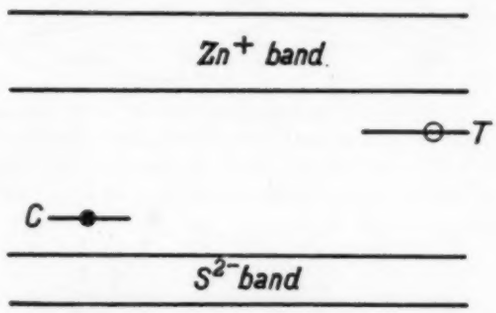

Fig. 1. Schematic energy diagram of a zinc sulfide phosphor containing two kinds of impurity levels; ● = electron and ○ = hole.

where *A* is the activator. The reverse process is responsible for the fluorescence.

One can thus understand why so many of the monovalent ions produce similar emissions in zinc sulfide, and why these emissions all shift in the same manner to longer wavelengths when cadmium is substituted for zinc. The small differences which still occur between the emissions of the various monovalent activator ions are probably caused by differences in the polarization and disturbance of the lattice around the activators.

So far it has been tacitly assumed that the activators and coactivators are distributed at random over the lattice positions. It is, however, also possible that they occupy neighboring lattice sites forming a kind of dipole within the lattice. The monovalent positive ion, forming one of the poles of such a dipole, must still raise the electronic level of a neighboring sulfur ion in the same way as was argued above for a separate activator ion. Arguments have been brought forward in support of either a dissociated or an associated center. The former is sup-

ported by the fact that the spectral distributions of silver, zinc, and copper-activated phosphors are independent of the nature of the coactivator (5). On the other hand, the fact that the line emissions of praseodymium and samarium are markedly different in the presence of different monovalent activators (5, 29) points at least to a partial association. Further experiments have to be carried out to clarify this point.

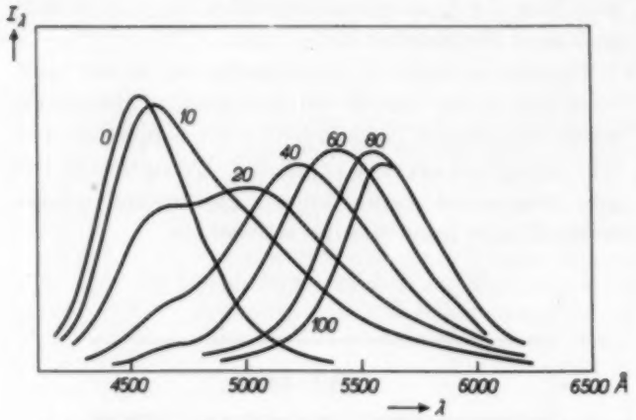

FIG. 2. Spectral distribution curves of a number of Zn(S, Se) phosphors activated with silver, fired at 900° in N_2, with 3% NaCl as flux. The numbers indicate the mole percentages of ZnSe. Excitation with 3650 Å at room temperature.

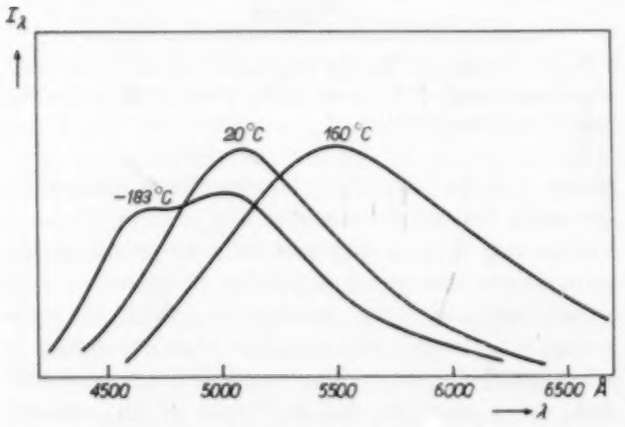

FIG. 3. Spectral distribution curves of Zn ($S_{0.8}$, $Se_{0.2}$)—Ag excited with 3650 Å at −183°, 20°, and 160°C.

It also remains to be explained why copper and gold may produce two different bands (2, 12–16).

Rothschild (12) attributes the green copper band to Cu^{2+} and the blue band to Cu^+, while Bube (15) is of the opinion that copper at interstitial places is responsible for the green band while the blue band is due to Cu^{2+} at lattice sites. Kröger and coauthors (5, 8), however, have shown that for the development of both the blue and the green copper bands chlorine or trivalent positive ions are necessary. These facts show that copper in both cases is present in the form of monovalent ions. To explain the two bands Kröger and coauthors (5, 16, 17) have assumed the green band to be due to Cu^+ ions and the blue band to Cu_2^+ ions.

Replacement of a sulfur ion by a trivalent negative ion must produce similar effects on the electronic levels of neighboring sulfur ions as the replacement of zinc by a monovalent positive ion. In this way the activation of zinc sulfide with phosphorus (6) and arsenic (18) may be explained.

Further support for the idea that impurity levels are to be attributed to disturbed sulfur ions comes from the emission of mixed crystals of sulfides and selenides activated with Zn^+ or Ag^+. The spectral distributions of a number of zinc sulfoselenides activated with silver are given in Fig. 2. They are very similar to the spectral distributions found by Leverenz (19). Substitution of selenium for sulfur not only shifts the bands to longer wavelengths, but causes

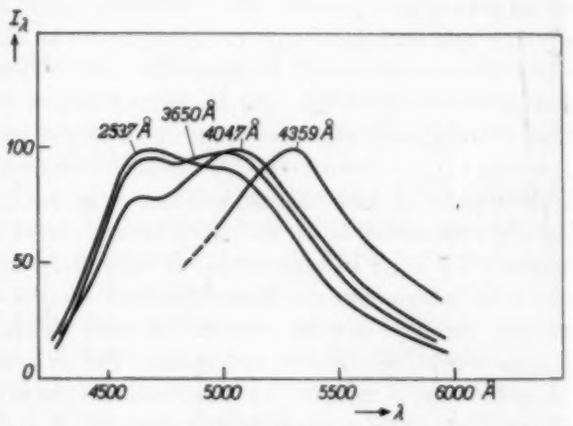

FIG. 4. Spectral distribution curves of Zn ($S_{0.8}$, $Se_{0.2}$)—Ag excited with 2537, 3650, 4047, and 4359 Å radiation at room temperature.

new bands to appear which are also shifted toward longer wavelengths with increasing selenium content. The appearance of these new bands may be understood when it is realized that two kinds of centers may then occur, e.g., disturbed sulfur and selenium ions. Increase of temperature or of the wavelength of excitation must favor the long-wave emissions caused by transitions of electrons from the conduction band to levels lying farther above the top of the occupied band. This effect is illustrated in Fig. 3 and 4.

It is remarkable that the blue and green copper bands behave quite differently. Both bands are shifted gradually to longer wavelengths with increasing selenium content and no new bands were found to appear.

Of the activators not yet mentioned manganese is most probably present in the form of its divalent positive ion because MnS and ZnS can form mixed

crystals over a large range. It is to be noted, however, that ZnS activated with Mn is hardly excited at all by ultraviolet radiation when fired in an atmosphere of pure H_2S (20). The characteristic yellow band only appears when HCl is added to the atmosphere or if aluminum is present. In the light of this evidence one might conclude that manganese is also present as a monovalent ion. On the other hand, firing with Al or HCl produces Zn^+ centers and it may well be that the excitation with 3650 Å takes place via these centers by some kind of energy transfer. ZnS-Mn without Cl is, moreover, easily excited with cathode rays.

The manganese emission seems to be characteristic of the ion itself. Substitution of zinc by cadmium or of sulfur by selenium has little effect on the spectral distribution as shown in Fig. 5 for the zinc sulfoselenides. Our results are markedly different from those of Leverenz (19). The curves of Leverenz,

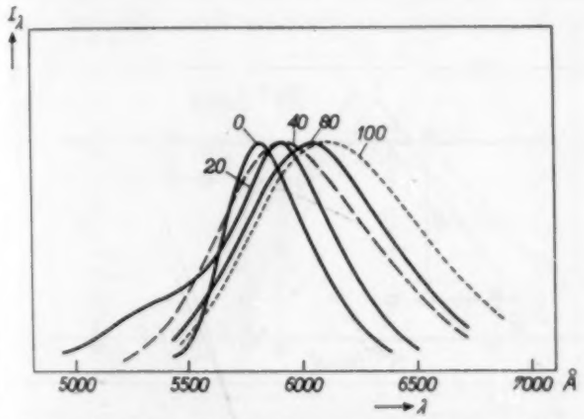

FIG. 5. Spectral distribution curves of a number of Zn(S, Se) phosphors activated with 0.5 mole % Mn, fired at 1000°C in H_2S + HCl. The numbers indicate the mole percentages of ZnSe; excitation with 3650 Å at −183°C.

however, show evidence of a strong zinc band which for small selenium contents is at the short-wave side of the Mn band and for high selenium content at the long-wave side. The broadening observed in our curves is no doubt also due to the appearance of the Zn band at higher selenium contents. Among the other activators which possibly are present in the divalent state are Pb and Sn. With the incorporation of Pb (21–24) two bands are produced. Since the presence of Cl^- seems to favor the green Pb band, Smit and Kröger (22) have attributed it to Pb^+. There are also indications that Sn (20, 25, 26) produces two bands.

Nature of Electron Traps

The arguments which have led us to believe that the monovalent activator ions replace Zn^{2+} ions at lattice sites also lead to the conclusion that the coactivators must occupy lattice sites. Replacement of Zn^{2+} by trivalent positive ions and substitution of S^{2-} by Cl^- involves the introduction of an extra positive charge. This extra positive charge must lower the electronic energy level of neighboring Zn^+ ions. Electrons moving freely through the lattice will be trapped near such a positive charge. The chemical equivalent of a filled trap in a phosphor containing Cl^- as coactivator might therefore be considered to be a Zn^+ ion next to a Cl^- ion, although the electron is probably shared by several Zn^{2+} ions around the Cl^- ion. The thermal release of the electron from such a trap may then be written:

$$(Zn^+Cl^-) + E \rightarrow (Zn^{2+}Cl^-) + \Theta.$$

Some idea of the magnitude of the dissociation energy or trap depth E may be obtained from a study of the thermal glow curve. This method, first applied by Urbach (27) to halides, was later used by

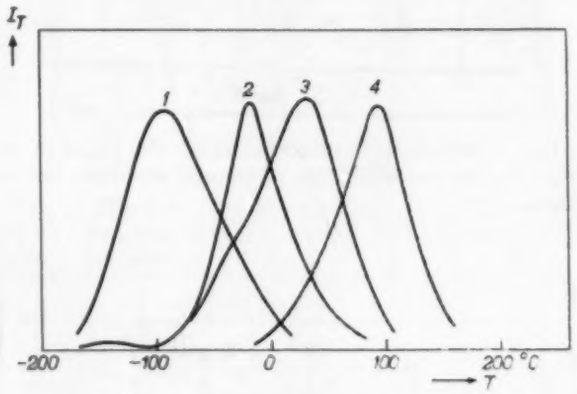

FIG. 6. Thermal glow curves for ZnS activated with Cu and different trivalent ions. (The activator concentration in Fig. 6, 8, 10, and 14 are in gram atom activator per mole ZnS.) Curve 1—ZnS − 5.10^{-5} Cu − 10^{-4} Al; curve 2—ZnS − 5.10^{-5} Cu − 10^{-4} Sc; curve 3—ZnS − 5.10^{-5} Cu − 10^{-4} Ga; curve 4—ZnS − 3.10^{-5} Cu − 3.10^{-5} In.

many others for the study of traps in zinc sulfide phosphors. The interpretation of these glow curves is difficult since nearly all published curves are rather complicated and often show many peaks. Hoogenstraaten (7), however, has shown recently that with sulfides made under carefully controlled conditions, using no flux and by firing in well defined atmospheres according to the method of Kröger (16), simpler glow curves are obtained. Oxygen must be avoided. Firing zinc sulfide in an atmosphere of H_2S and HCl, one obtains a single glow peak at approximately −90°C regardless of the nature of the activator. With trivalent ions, other characteristic glow peaks are obtained as shown in Fig. 6. This is just what one would expect, if the coactivators are responsible for unoccupied levels below the conduction band.

Riehl (28) has suggested that such levels may be filled directly with electrons from the occupied band

(transition [1] of Fig. 7), for example by excitation with 3650 Å radiation. In that case there seems to be no reason why the reverse process—the recombination of a free hole with a trapped electron—should not occur with emission of light. This transition is indicated by transition [2] in Fig. 7 where the hole recombines directly with the trapped electron, or by transition [2a] if it passes through a "waiting state." Three of the trivalent coactivators Sc, Ga, and In have indeed been found (5) to be associated with broad emission bands. The theory that these

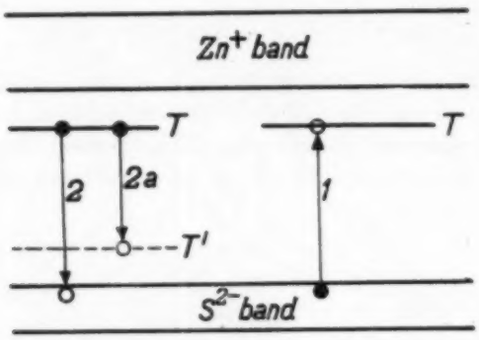

FIG. 7. Schematic representation of the emission produced by the recombination of trapped electrons and free holes.

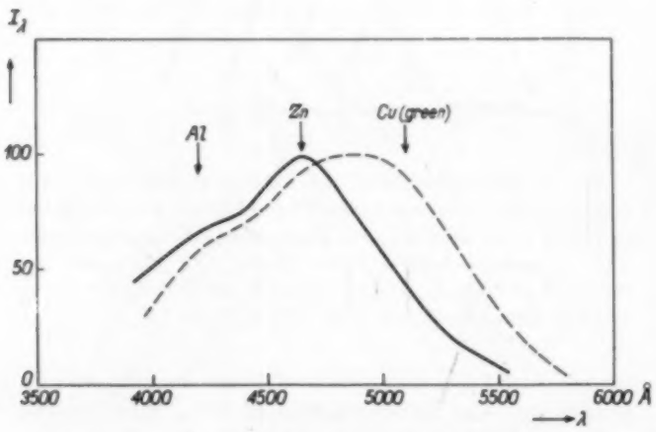

FIG. 8. Spectral distribution curves of zinc sulfide phosphors showing the aluminum band. Curve 1—ZnS fired with 10^{-4} Al at 1200° in H_2S; curve 2—ZnS − 10^{-3} Al − 5.10^{-6} Cu fired at 1300° in H_2S. Excitation with 3650 Å at −183°C.

emissions are due to transitions [2] or [2a] is supported by the fact that those ions which are responsible for the deepest traps also produce the reddest emissions. One would also expect Al to give an emission band, probably in the blue region, because of its shallow trap. Indications of an Al band have indeed been found on the short wavelength side of the Zn band in zinc sulfides fired with an excess of aluminum, as shown in Fig. 8. It is seen from the above that traps may also function as luminescent centers and that a distinction has therefore to be made between two types of centers in zinc sulfide phosphors. The various excitation and emission processes of these two types are indicated schematically in Fig. 9. We have:

1. *Centers represented by occupied levels C.*—On excitation some of these levels lose an electron by direct absorption [3] or by capturing a hole from the occupied band [8]. Such a hole may be obtained by lifting an electron from the full band into the conduction band [9]. Emission occurs when free electrons from the conduction band recombine with holes in *C*-levels [4]. Temperature quenching of the emission starts at temperatures where electrons may be lifted thermally from the occupied band into the empty *C*-levels or, in other words, when the holes in *C*-levels are transferred thermally to the occupied band [7].

2. *Centers represented by unoccupied levels T.*—In the excited state these levels are occupied by electrons. Excitation may occur through direct absorption [1] or by capturing an electron from the conduction

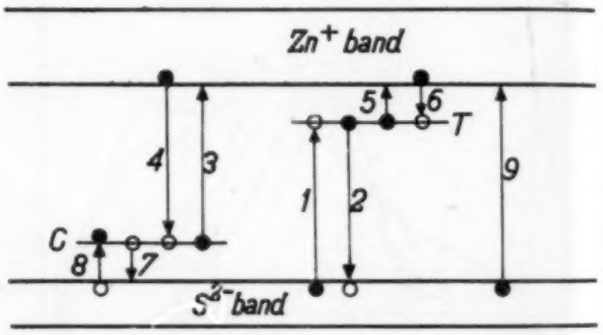

FIG. 9. Schematic representation of various transitions in a ZnS phosphor.

band [6]. Emission is indicated by [2]. Thermal quenching starts when electrons are lifted thermally into the conduction band [5]. "Waiting states" which may be present in both types of centers have been omitted for simplicity.

Consider now the effects of cadmium and selenium substitution on the *T*-levels. It has already been seen that cadmium substitution shifts the emission connected with the *C*-levels to longer wavelengths by an amount about equal to the shortening of the distance between the S^{2-} and Zn^+ band, as judged from the shift of the fundamental absorption edge. It seems, therefore, that the conduction band moves down with respect to the occupied band without affecting greatly the distance between *C*-levels and the latter. This is confirmed by a study of the temperature quenching of (Zn, Cd)S phosphors. The temperature of quenching is not lowered much by the substitution of zinc by cadmium. The distance between the *T*-levels and the full band is apparently also little affected by the cadmium substi-

tution. This is evident from the spectral distribution of (Zn, Cd)S activated with indium (Fig. 10). The peak moves from 6100 to 6200 Å when the cadmium content is increased from 0 to 20 per cent. This corresponds to a decrease in energy of only 0.03 ev. Also, the scandium band at 5400 Å was found to be little affected by the cadmium substitution.

Since the gap between the conduction and the occupied band becomes smaller, the distance between T and the conduction band should diminish when cadmium is substituted for zinc. This was confirmed by Hoogenstraaten (7), who found indeed that the trap depth of various traps was lowered at a rate only slightly less than the rate at which the distance between the two bands is diminished. Another remarkable effect found by Hoogenstraaten was the appearance of new traps in zinc sulfide phosphors containing Cl^- or Al^{3+} as coactivators when zinc was gradually replaced by cadmium. This is in accordance with our theory that the traps are to be considered as disturbed cations. When the lattice contains both Zn^{2+} and Cd^{2+} ions, traps of different depth may be found depending on whether Cd^{2+} or Zn^{2+} ions, or possibly various combinations of these ions, are disturbed. This phenomenon is to be compared with the appearance of new emission bands in the spectra of zinc sulfide activated with Ag^+ when sulfur is partly replaced by selenium. Also in accordance with our theory is the fact that the selenium substitution does not produce new traps. Fig. 11 and 12 show that the Cl^- and Al^{3+} peaks in the glow curves are merely shifted to lower temperatures; no new peaks are observed in contrast to the phosphor with cadmium substitution. To follow the shifts to very low temperatures, it was necessary to cool the phosphor in liquid hydrogen. A new shallow trap was thereby observed giving a glow peak at 60°K which is not affected by the selenium substitution. The nature of this shallow trap has not been established. The Cl^- and Al^{3+} peaks move to lower temperatures with increasing selenium content until they merge into this low temperature peak.

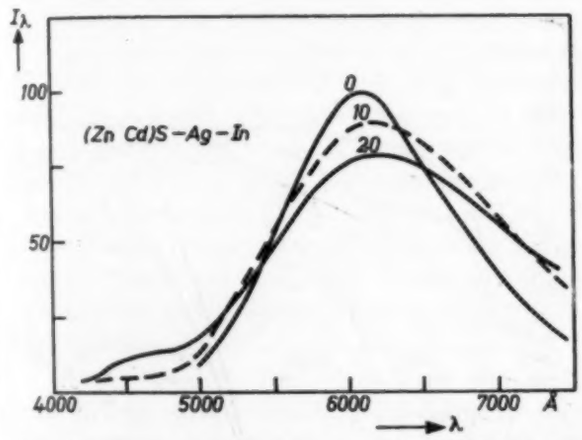

FIG. 10. Spectral distribution curves for (Zn, Cd)S fired with 5.10^{-5} Ag + 10^{-4} In at 1100°C in H_2S. Excitation with 3650 Å at −183°C.

Some of the trivalent ions active in zinc sulfide do not belong to the class of indirect activators. Samarium produces a line emission while cerium shows the double-peaked emission characteristic of all cerium activated phosphors. However, one property is found in cerium-activated zinc sulfide which is characteristic for zinc sulfide phosphors and which arises from the fact that the emission is a recombination process, namely, that the quenching temperature is a function of the intensity of the exciting radiation (5). We have therefore come to the conclusion that the first stage in the emission process of cerium is a recombination process indicated by transition [2] in Fig. 9—the Ce^{3+} ion must produce T-levels—and that the energy released by this process is transferred to the activator itself bringing it into an excited

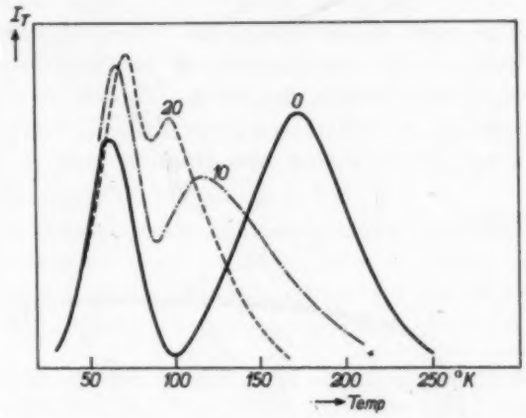

FIG. 11. Thermal glow curves of Zn(S, Se) activated with 3.10^{-5} Cu and fired in HCl at 1000°C. The numbers indicate the mole percentages of ZnSe.

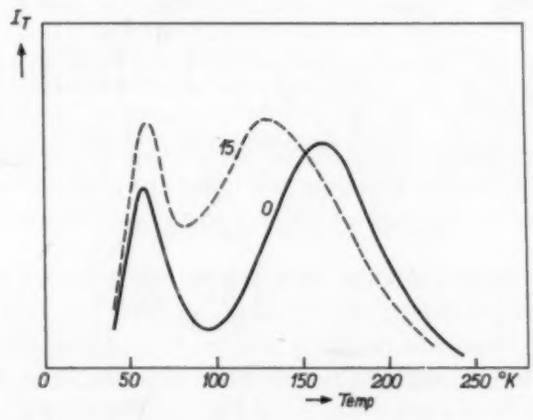

FIG. 12. Thermal glow curves of Zn(S, Se) activated with 3.10^{-5} Cu and 3.10^{-5} Al and fired in N_2 + CS_2 at 1000°C. The numbers indicate the mole percentages of ZnSe.

state. The process of emission may then be represented as:

$$(Zn^{+}Ce^{3+}) + S^{-} \rightarrow (Zn^{2+}Ce^{3+*}) + S^{2-}$$

followed by

$$Ce^{3+*} \rightarrow Ce^{3+} + h\nu.$$

Quenching of the emission probably occurs at temperatures where the electrons trapped in the T-levels belonging to the cerium center are released again by thermal agitation. On the other hand, quenching may be a property of the activator itself. This is found to occur in the ions of the iron group known as "killers." No coactivators are necessary to incorporate these ions in the zinc sulfide lattice. They are situated as divalent ions at normal Zn^{2+} positions in the lattice. Since they also produce traps (7, 33)

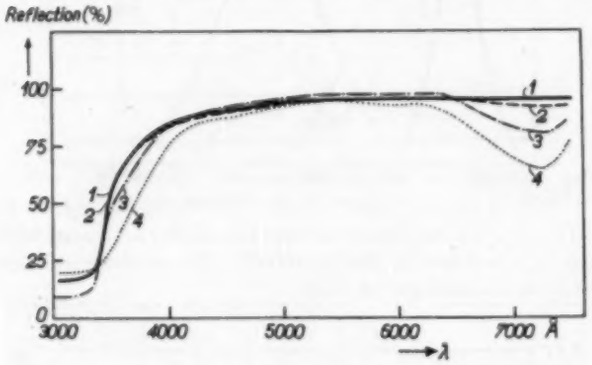

FIG. 13. Reflection spectra of ZnS—Co. Curve 1—0 Co; curve 2—10^{-6} Co; curve 3—10^{-5} Co; curve 4—10^{-4} Co.

the electronic levels of Ni^{+} and Co^{+} must be below the Zn^{+} band. Trapping can then be represented as:

$$Zn^{+} + Ni^{2+} \rightarrow Zn^{2+} + Ni^{+}.$$

Both killers produce new absorption bands at the long-wave side of the lattice absorption (Fig. 13 and 14). These are probably related to a direct filling of the Co^{+} and Ni^{+} levels with electrons from the filled band (transition [1] of Fig. 9). The absorption caused by nickel extends further into the visible due to its greater trap depth. Both ions show also characteristic absorption in the red region.

According to the well-known Mott-Seitz theory, radiationless transitions from an excited state to a lower state may occur at relatively low temperatures when the potential energy curves for the two states plotted against a generalized configurational coordinate cross at a point not too far above the minimum of the curve of the higher state. This is the more likely to occur the smaller the energy difference between the two states. Both the Ni^{2+} and the Co^{2+} ions have a partially filled third shell. Many combinations of the orbital and spin moments are possible and the energy differences between the various combinations are not great. When, therefore, the energy released by transition [2] ($S^{2-} + Ni^{+} \rightarrow S^{-} + Ni^{2+}$) is transferred to the Ni^{2+} ion itself, bringing it into one of the excited states, it is not surprising that the ion returns to the ground state via a number of radiationless transitions to intermediate states. The killers can thus be considered to be activators with a low quenching temperature. That they are sometimes also capable of emitting light is shown by the fluorescence of MgO — Ni (30) and ZnS — Fe (31).

Interaction between C- and T-Levels

We have distinguished above between two kinds of impurity levels in zinc sulfide phosphors. The C-levels are normally occupied by electrons and the T-levels are normally empty. In the excited state this situation is partly reversed. Since both types of levels are usually present in zinc sulfide phosphors, several processes indicated by transitions [1 to 9] in

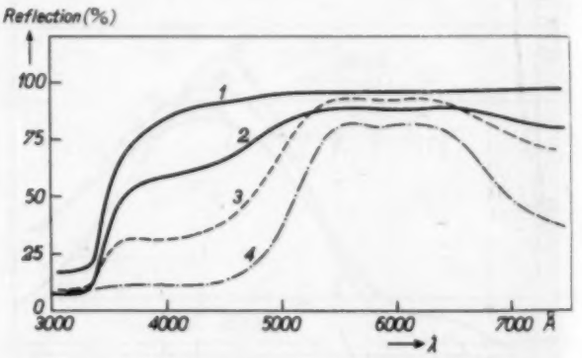

FIG. 14. Reflection spectra of ZnS—Ni. Curve 1—0 Ni; curve 2—10^{-5} Ni; curve 3—10^{-4} Ni; curve 4—10^{-3} Ni.

Fig. 9 may happen simultaneously. Which process dominates depends on the rates of the various transitions. The temperature which determines the rates of transitions [5] and [7] is an important factor. If [5] or [7] are too fast, the corresponding emissions [2] and [4] do not take place. Interaction between the two centers may occur when electrons are liberated from T-levels and recombine with empty C-levels, or when holes are transferred from empty C-levels and recombine with occupied T-levels.

The rate of process [5] or [7] is determined by a temperature-dependent factor $\gamma = s \exp(-E/kT)$, where s is a constant and E the distance between the levels and the nearest band. Whether energy will be transferred from C to T or vice versa is determined mainly by the ratio of the γ factors of processes [5] and [7]. This may be illustrated by a few examples.

ZnS—Cu—Co: The glow curve of this phosphor shows a peak at 380°K which is characteristic for Co (7, 32, 33). At that temperature, electrons are released

from the Co traps and recombine with the empty Cu levels.

ZnS—Ag—Co: The distance between C and the occupied band is smaller in Ag activated than in Cu activated sulfides. Now the peak at 380°K is not observed. Instead, the glow at higher temperatures is reduced, because holes move away from the empty Ag levels to recombine without radiation with electrons trapped in the Co traps.

ZnS—Ag—Sc: Scandium gives a characteristic peak in the glow curve. The color of the emission during the thermal glow is blue. Energy is transferred from T to C.

ZnS—Ag—In: The In trap is deeper than the Sc trap. The color of the emission during thermal glow is yellow. Now the energy transfer is from C to T.

Transitions [5] and [7] can also be stimulated optically. Antonov-Romanovskii and Shchukin (34) found new absorption bands with maxima at 13,000, 8000, and 4500 Å in a ZnS—Cu—Co phosphor during excitation. The first two bands are also found in the stimulation spectra of ZnS—Cu—Pb and ZnS—Cu—Mn (13, 35) and in the quenching spectrum of ZnS—Cu—Co (36). They are a property of the excited Cu center and probably correspond to transition [7]. The fact that two bands are observed indicates an intermediate level between C and the full band. Thermal energy is required to bring the hole from this band to the full band. Fonda (35), indeed, observed that at 77°K stimulation only occurs in the 8000 Å band.

The release of electrons from traps may also be produced optically. Infrared radiation causes stimulation in most Cu activated sulfides at low temperatures where transition [7] is sufficiently reduced. Even the exciting radiation may liberate trapped electrons. This is shown by the results of Smith and Turkevich (38) who found a marked effect of the wavelength of excitation on the thermal glow curve, while Hoogenstraaten and Klasens (32) have deduced from the properties of ZnS—Cu—Co phosphors that electrons trapped by the Co traps are ejected again by 3650 Å radiation.

Infrared radiation and increase of temperature often show the opposite effects. In ZnS—Cu—In the afterglow is green and increases in intensity when the temperature is raised. The electrons go from the In traps through the conduction band to the empty C-levels due to Cu. If, however, during the afterglow the phosphor is exposed to infrared radiation, the green emission is quenched while the yellow indium emission is stimulated. Now the holes go from the empty C-levels through the occupied band to recombine with the electrons in In traps. A similar mechanism has been proposed for SrS—Ce—Sm by Kröger (39), Urbach (40), and Brauer (41). In this phosphor, heating after excitation produces the Sm-emission, while with infrared radiation the Ce-emission is stimulated.

In phosphors emitting two bands, one belonging to a level C and another to a level T, quenching of one emission will generally stimulate the other. Such phenomena were already observed by Lenard (42) with CaS—Bi phosphors. The maxima in the stimulation spectrum of the β emission (5030 Å) were found to coincide with the maxima in the quenching spectrum of the α band (4740 Å). Many more examples may be given to illustrate the above theory of energy levels and energy transfer in zinc sulfide phosphors. On the other hand, no doubt other cases may be brought forward, for example the fact that zinc sulfoselenides activated by Cu behave differently from zinc sulfoselenides activated by Ag, where this simple theory seems to fail.

It is firmly believed, however, that such apparent exceptions, when better understood after further research, will call for modification or refinement rather than for a total rejection of the present theory.

Any discussion of this paper will appear in a Discussion Section, to be published in the December 1953 issue of the JOURNAL.

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Optical Measurements on Electroluminescent Zinc Sulfide[1]

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ABSTRACT

Absorption and emission spectra of electroluminescent ZnS phosphors, activated by Cu and Pb, are reported. Three absorption bands are observed, at 3.18 electron volts (ev), at about 2.7 ev, and somewhere below one ev. The infrared absorption band is associated with the Pb activator but its exact location is uncertain. The emission spectra of both blue and green phosphors may be resolved into the same emission bands, at 2.15, 2.4, and 2.7 ev, respectively. The primary difference between the spectra of blue phosphors and green phosphors lies in the ratio of the amplitudes of the green and blue bands. This ratio is also shown to be a function of the frequency of the applied alternating field, but is independent of the magnitude of the field.

INTRODUCTION

The measurements described in this report were made primarily to furnish information which would be helpful in developing a theory of the mechanism of electroluminescence (1, 2). They were made on zinc sulfide phosphors, activated with about 10^{-3} moles Cu and 10^{-5} moles Pb per mole of ZnS. $ZnCl_2$ was used as the fluxing agent in these phosphors. The percentage of ZnO in the finished phosphors is believed to be extremely small. The measurements may be divided into two categories: measurements of the optical absorption of the phosphors, and measurements of the energy distribution of the radiation emitted from the phosphors when excited by electroluminescence.

OPTICAL ABSORPTION

Since these phosphors are in the form of fine powders, the measurements of the optical absorption were performed using a diffuse reflection technique. This was done with the diffuse reflection apparatus which may be purchased for use with the Beckman Model DU spectrophotometer. With this apparatus, the reflectance of a powder sample is measured by comparing the amount of light diffusely reflected from its surface with that reflected from the surface of a "standard white" powder, which was in this case basic magnesium carbonate. Measurements of reflectance of the phosphors were made in this way between 10,000 and 3500 Å.

Since these phosphors fluoresce under excitation by radiation in the far blue and near ultraviolet, a filter with a cutoff at 4100 Å was used to separate fluorescent emission from the reflected light for wavelengths of the incident radiation less than 4250 Å. In this way, curves of true reflectance could be obtained as a function of wavelength.

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Fig. 1 illustrates the type of curves which are obtained. The upper of the two curves is for ZnS, while the lower is for a typical green phosphor. Obviously, the phosphor shows the presence of additional absorption bands which must be due to the presence of activators. To show up the location of these bands more definitely, the analysis shown below is employed.

The basic assumption is that the reflected light has travelled on the average a distance, D, through the powder; its reflection coefficient will therefore be given by:

$$R_p \propto \exp(-[\sigma_A + \sigma_M]D), \qquad \text{(I)}$$

where σ_A is the absorption coefficient due to the activators and σ_M is the absorption coefficient due to the matrix. Similarly the reflection coefficient of ZnS will be given by:

$$R_Z \propto \exp(-\sigma_M D). \qquad \text{(II)}$$

By a separate measurement of the reflectance of ZnS, $\exp(-\sigma_M D)$ can be determined; thus, by division of phosphor reflectance by ZnS reflectance and subtraction of the quotient from unity the following expression is obtained,

$$A = 1 - R_p/R_Z = 1 - \exp(-\sigma_A D), \qquad \text{(III)}$$

which is then called "the absorption due to the activators."

Fig. 2 shows typical curves of absorption due to activators plotted as a function of photon energy for a typical green phosphor. There appears to be a major absorption band centering at 3.18 ev (3900 Å), a minor absorption band in the neighborhood of 2.7 ev (4600 Å), and a third absorption band centering somewhere below 1 ev. The location of the infrared band is uncertain, since the monochromator could not be used beyond 12,000 Å (1.03 ev), but it is estimated as lying in the neighborhood of 0.8 ev. Absorption curves for blue phosphors are very simi-

lar to those shown for the green; the same three absorption bands are present in both. The 3.18 ev band is much weaker in blue phosphors than in green phosphors; this observation is valid enough so that blue phosphors may be identified by their absorption curves.

The infrared absorption band which is found in the absorption spectrum has been assigned to the Pb activator, as is shown in Fig. 3. In this figure, the absorption at 1.03 ev is plotted against the

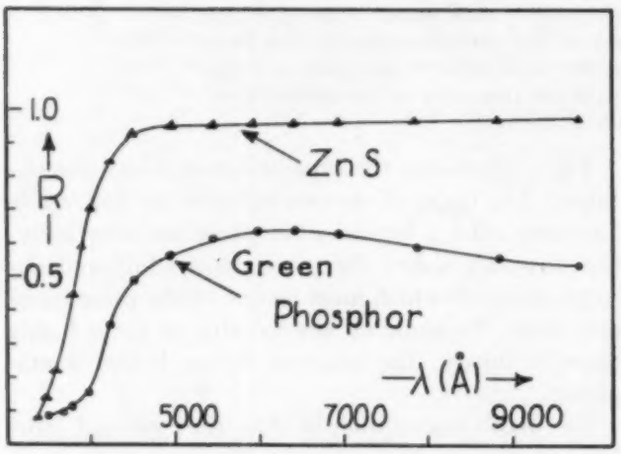

FIG. 1. Reflectance vs. wavelength

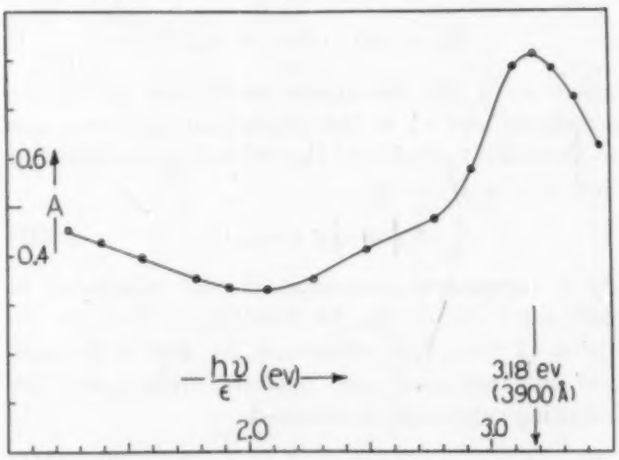

FIG. 2. Absorption due to activators vs. energy of photons (green phosphor).

logarithm of the concentration of Pb found by chemical analysis in the phosphor. For concentrations less than 4×10^{-3} per cent Pb by weight, the absorption and Pb concentration are well correlated. At higher concentrations than 4×10^{-3} per cent, there is no correlation. It has been suggested that at higher concentrations of Pb, crystals of galena (PbS) form, and that these rob the ZnS lattice of dissolved Pb. Some evidence has been found by x-ray analysis for the presence of PbS in some of these high-Pb phosphors, but it is as yet inconclusive.

SPECTRAL ENERGY DISTRIBUTION

The energy distribution of the radiation emitted from a number of phosphors has been measured, as an alternative means of gaining information about the energy level scheme of the phosphor. This measurement was made using a Beckman monochromator

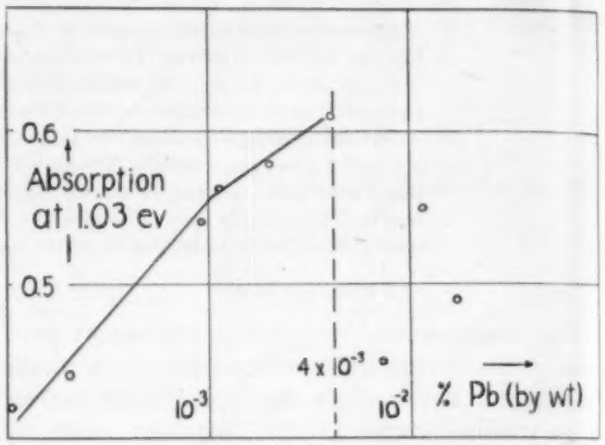

FIG. 3. Infrared absorption vs. Pb concentration

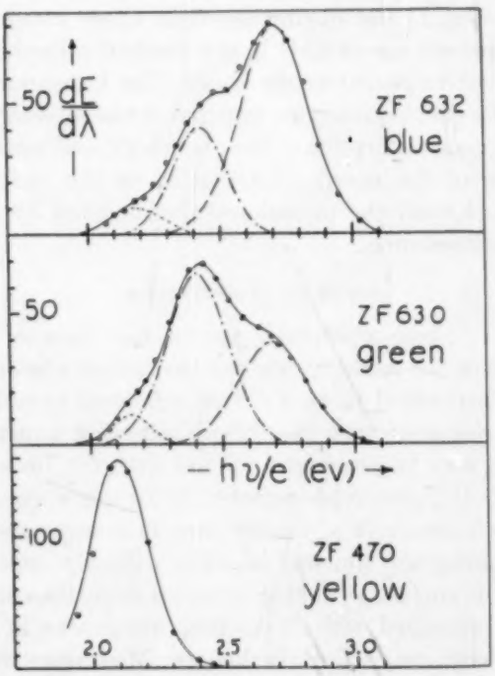

FIG. 4. Spectral energy distribution as a function of photon energy (blue, green, and yellow phosphors).

with a 1P21 photomultiplier as a detector. The system was calibrated using a fluorescent lamp of known spectral energy distribution as a secondary standard. Care was taken to exclude stray radiation of shorter wavelength than the monochromator setting from the beam emergent from the exit slit by means of a series of sharp cutoff filters.

Fig. 4 shows curves of the energy distribution of the radiation emitted from three different phosphors

plotted as a function of photon energy. In these curves, therefore, blue is at the right hand side of the diagram and red is at the left. The ordinate is in arbitrary units. These curves are not necessarily typical; this green phosphor has a good deal more blue than is normal. It was chosen for the purpose of illustration here for that very reason, so as to emphasize the presence of the blue band in the emission spectrum of green phosphors. The solid curve is in each case the sum of the Gaussian bands, which are shown as dotted and dashed lines. The circles are the experimental points. It is evident that the points are well represented by the synthesized solid curves.

The emission spectra of both green and blue phosphors are composed of the same three bands, at

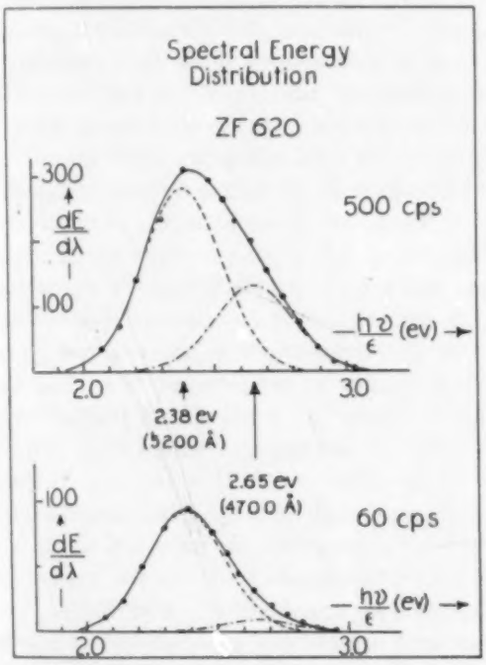

FIG. 5. Spectral energy distributions for a green phosphor at 60 and 500 c.p.s.

about 2.7, 2.4, and 2.15 ev, respectively. The primary difference is in the ratio of amplitudes of green and blue bands. It is interesting to note that the curves of spectral energy distribution of green and blue phosphors excited by 3650 Å ultraviolet radiation are composed of the same emission bands as when the phosphors are excited by electroluminescence. The ratio of green to blue is always smaller when the phosphor is excited by ultraviolet. In the curve for the yellow phosphor which is plotted here, only a single band, centering at 2.10 ev (5900 Å), is observed.

Fig. 5 shows the result of measurements of spectral energy distribution of a typical green phosphor at two different frequencies of exciting alternating field. The ratio of amplitudes of the green and blue bands is about 10:1 at 60 c.p.s., while at 500 c.p.s. it is about 2:1. Since the bands are quite broad, the change in the over-all distribution appears at first glance to be merely a shift of modal energy. Fig. 6 shows the variation of the amplitudes of the green and the blue bands with frequency of exciting alternating field.

The amplitude of the blue band increases almost linearly with frequency, while that of the green band saturates at about 1000 c.p.s. This can only be the case if the time required to "activate" blue centers is very much shorter than the shortest period encountered (5×10^{-4} sec), so that the same number of blue centers are active each cycle, and the total emission from them is proportional to the number of cycles per second. By similar reasoning, it is concluded that the time required to activate green centers is comparable with 5×10^{-4} sec.

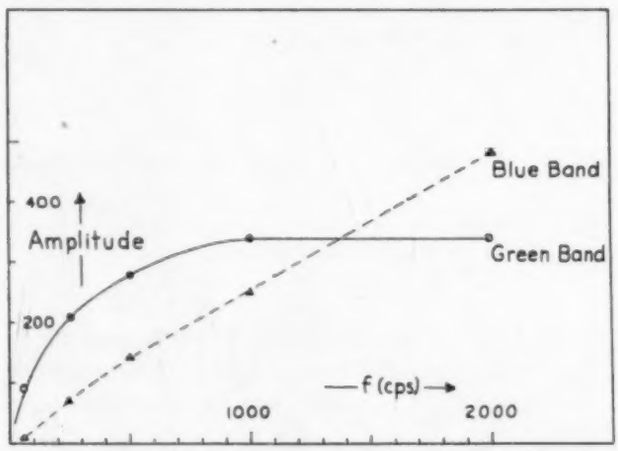

FIG. 6. Variation of amplitude of emission bands with frequency of excitation (green phosphor).

The dependence of spectral energy distribution on applied field has also been investigated with the following results. Over a range of brightnesses represented by a factor of 2.5 (the same range as covered by Fig. 5), the spectral energy distribution was independent of the applied field.

SUMMARY

1. Green and blue electroluminescent zinc sulfides show substantially the same absorption bands, e.g., 3.18 ev, about 2.7 ev, and about 0.8 ev or less.

2. The 0.8 ev absorption band is associated with the Pb activator.

3. Blue and green phosphors show the same major emission bands, e.g., 2.70 ev, 2.40 ev.

4. Increased emission in the higher energy emission band (2.70 ev) is paralleled by decreased absorption in the higher energy absorption band (3.18 ev). This correlation is good enough so that blue phos-

phors may be readily identified from their absorption curves.

5. The ratio of the amplitude of the green band to that of the blue band is a function of frequency.

Acknowledgments

The author is indebted to his colleagues in the Engineering Laboratories for many helpful suggestions and consultations, in the course of the measurements themselves as well as in the preparation of the manuscript of this paper.

Any discussion of this paper will appear in a Discussion Section, to be published in the December 1953 issue of the Journal.

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Acid Dissociation of the Aquoscandium Ions[1]

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ABSTRACT

A study of the hydrogen ion concentrations of scandium perchlorate solutions to which sodium hydroxide has been added reveals that the data cannot be explained by assuming a single acid dissociation step. The data can be interpreted in terms of a single acid dissociation followed by dimerization of the base conjugate to the hexaquo ion. In the solvent salt sodium perchlorate at a concentration of one molar, K for the first step is equal to 1.17×10^{-5}, with the K for the dimerization equal to 7.38×10^{3}. The literature indicates that this may be a general phenomenon.

INTRODUCTION

As early as 1907, studies of the structure of metal hydroxides, hydrous oxides, and basic salts led to the conclusion that these species may be polymeric (1). Thomas has explained the properties of the hydrous oxides in colloidal systems in terms of polynuclear metal ions, using the idea of dihydroxy or diol bridges employed earlier by Werner and Pfeiffer (2). While most chemists today recognize the complications in aqueous chemistry due to formation of various types of complexes and of ion pairs, metallic cations are usually assumed to be monomeric (3, 4). However, examination of the precipitated basic salts or hydrous oxides on addition of sodium hydroxide has demonstrated that there are usually dimers or higher polymers in the solid phase. It is one of the purposes of this paper to demonstrate that the hydrated scandium ion also forms dimers and polymers in solution as has been shown recently by Pedersen (5) for copper nitrate, by Graner and Sillén (6) for bismuth perchlorate systems, and by Ahrland (7) for uranyl ion in aqueous perchlorate systems; and further that no mass law expression which does not include the formation of polymers can successfully describe the systems studied.

EXPERIMENTAL METHOD

The system chosen for study was aqueous scandium perchlorate where the hexa-aquoscandium ion is partly reacted with hydroxyl ion. The coordination number of six is assumed for the scandium aquo ion. It will be shown that the experimental results cannot be explained on the basis of the equilibrium

$$\underset{Sc_0}{[Sc(H_2O)_6]^{3+}} + H_2O \rightleftarrows \underset{Sc_1}{[Sc(H_2O)_5OH]^{2+}} + H_3O^+ \qquad (I)$$

nor

$$\underset{Sc_1}{[Sc(H_2O)_5OH]^{2+}} + H_2O \rightleftarrows \underset{Sc_2}{[Sc(H_2O)_4(OH)_2]^{+}} + H_3O^+ \qquad (II)$$

or a combination of the above equilibria. However, the experimental data appear to be consistent with a combination of (I) and (III)

$$\underset{Sc_1}{2[Sc(H_2O)_5OH]^{2+}} \rightleftarrows \underset{Sc_{2,4}}{[Sc(H_2O)_5OH]_2^{4+}} \qquad (III)$$

The experimental method was the determination of hydrogen ion concentration in buffers of known stoichiometric composition in the solvent salt sodium perchlorate in swamping concentrations.

The hydrogen ion concentrations were determined by a modification of the method used by Kilpatrick and coworkers (8), with the additional assumptions that the scandium ion does not complex with perchlorate nor with quinhydrone. The second assumption seemed justified by the fact that absorption patterns for the scandium-quinhydrone systems showed no bands indicating complexes.

The emf of the cell

$$Au \left| \begin{matrix} HClO_4 \\ NaClO_4 \\ Quinhydrone \end{matrix} \right\| NaClO_4 \left\| \begin{matrix} Sc(ClO_4)_3 \text{ buffer} \\ NaClO_4 \\ Quinhydrone \end{matrix} \right| Au$$

was measured using a Type K-2 potentiometer with suitable galvanometer.

[1] Manuscript received July 21, 1952. This paper was prepared for delivery before the Philadelphia Meeting, May 4 to 8, 1952.

[2] This paper was abstracted from a part of the dissertation presented by Lewis Pokras to the Faculty of the Graduate School of the Illinois Institute of Technology in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

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Chemicals

Sodium perchlorate was prepared from primary standard grade sodium carbonate and vacuum-distilled 70–72 per cent perchloric acid in approximately stoichiometric proportions. The product was recrystallized at least three times from distilled water. Concentrated stock solutions (ca 4*M*) were prepared as needed and standardized by precipitation of the perchlorate as tetraphenyl arsonium perchlorate salt. The analytical method is a variation of the tetraphenyl phosphonium perchlorate procedure of Willard, as modified by Hunt (9).

Scandium perchlorate hydrate was prepared by dissolving the purified oxide in excess perchloric acid and recrystallizing from perchloric acid and water (10). Microscopic examination of the product indicated it to be crystalline. The product was highly hygroscopic, having a vapor pressure of 2 to 3 mm

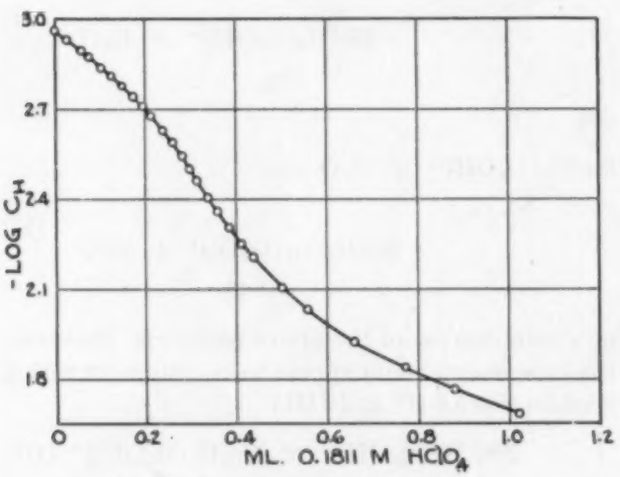


FIG. 1. Titration of 0.100$_0$*M* $Sc(ClO_4)_3$

at 25°C. Spectrographic examination indicated only traces of various impurities including the rare earths, with approximately 0.06 per cent yttrium. The sample was analyzed for scandium by the oxine method (11) and for perchlorate. All determinations were carried out in triplicate, the average deviation from the mean being ±0.4 per cent for scandium and ±0.3 per cent for perchlorate.

During the course of the work, four lots of scandium perchlorate were prepared with ratios of perchlorate to scandium, *a*, of 2.933, 2.059, 2.026, and 2.906 ± 0.5 per cent. Three recrystallizations of a portion of lot 4 from water gave a product which showed a ratio of 2.738. Apparently the solid product is not necessarily the pure hexahydrate, Sc_3, but may be a mixture of Sc_3 and Sc_2 perchlorates where the ratio *a* is 2. These results are entirely consistent with the observations of Sterba-Böhm and Melichar (12) that basic formates can be obtained by repeated slow recrystallization of the normal salt from aqueous solutions.

A stock solution of lot 4 was prepared and the base, Sc_2, titrated with perchloric acid using a microburette. All reagent solutions involved were made up to an ionic strength of 1 with $NaClO_4$. Fig. 1 presents the titration curve and Fig. 2 gives the end point by the method of MacInnes (13). This end point yields a calculated *a* value of 2.973; and for lots 1, 2, and 3, values of 2.978, 2.066, and 2.051, respectively.

Preparation of Buffer Solutions

The solutions were prepared by mixing measured volumes of standardized stock solutions of scandium perchlorate, carbonate-free sodium hydroxide, perchloric acid, sodium perchlorate, and distilled water.

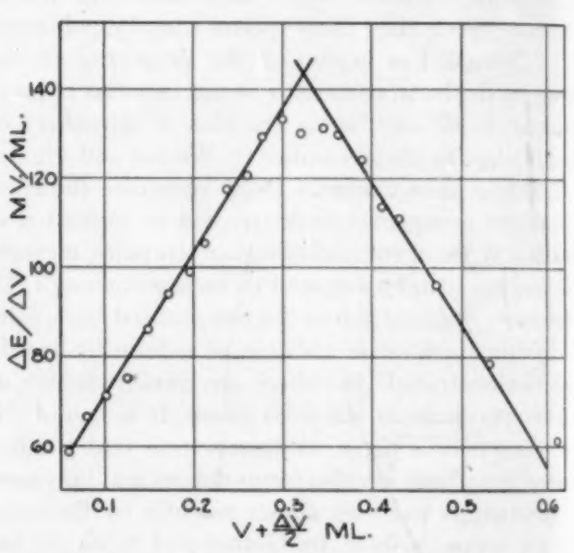


FIG. 2. Differential titration plot for 0.100$_0$*M* $Sc(ClO_4)_3$

The results of the experimental study are expressed in terms of hydrogen ion concentration and the stoichiometric composition of the solutions. In order that the data shall not reflect additional assumptions concerning the species present in the solution, the compositions of the buffers have been expressed in terms of *C*, the stoichiometric scandium concentration in moles per liter, and the parameter *n*. This parameter is the hydroxyl number, the stoichiometric ratio of moles OH^- per gram atom of scandium

$$n \equiv (3 - a) + \frac{C_{NaOH} - C_{HClO_4}}{C} \qquad \text{(IV)}$$

where *a* is the ratio of perchlorate to scandium in the solid scandium perchlorate sample employed to prepare the stock solution.

Table I gives a typical experiment which shows the reproducibility of the results, and Fig. 3 shows

the logarithm of the hydrogen ion concentration as a function of n for different stoichiometric concentrations of scandium. For values of n between 0.3 and 1.0 there is essentially a linear relationship and the results can be represented by equations of the form

$$-\log C_H = A + Bn. \qquad (V)$$

The values of A and B are given in Table II.

The linear relationship noted here is in itself only a convenient empirical means of calculating $-\log C_H$ values for scandium perchlorate solutions of known

TABLE I. *Measurements with scandium perchlorate buffers at 25°C*

Composition of scandium solution:

Ionic strength, μ 1.000 — Stoichimetric molarity: Total Sc 2.000×10^{-2}
Ratio ClO_4/Sc, a 2.973 — NaOH 1.000×10^{-2}
Hydroxyl No., n 0.527 — $NaClO_4$ 0.915

Cell: Au | 9.061×10^{-3} *M* $HClO_4$, 0.991 *M* $NaClO_4$, Quinhydrone || 4.12$_5$ *M* $NaClO_4$ || 9.46×10^{-3} *M* Sc_3, 1.054×10^{-2} *M* Sc_3, 0.915 *M* $NaClO_4$, Quinhydrone | Au

Trial	Time min	Electrode pair	EMF mv	EMF avg	a.d.
1	11	1–4	108.23		
		2–4	108.23		
		2–3	108.25		
		1–3	108.25		
		1–2	0.00		
	13	3–4	−0.01	108.24	0.01
2	20	1–4	108.27		
		2–4	108.28		
		2–3	108.29		
		1–3	108.29		
		1–2	0.00		
	23	3–4	0.00	108.28	0.01
3	30	1–4	108.33		
		2–4	108.33		
		2–3	108.34		
		1–3	108.34		
		1–2	0.00		
	33	3–4	−0.01	108.33	0.00$_5$
		1–3		108.28	0.03

RT/F ln (avg emf) = 1.8310, $-\log [H_3O^+] = 3.8738$

stoichiometric composition. However, in conjunction with the observed dependence of C_H on C, the linearity demonstrates that the acid involved does not obey monoprotic, diprotic, or triprotic acid mass-law relationships.

The Monoprotic Treatment

If one assumes that the aquoscandium ion Sc_3 acts as a monoprotic acid as given in equation (I), the equilibrium constant formulated in terms of measured parameters may be written as

$$K_1 = \frac{C_H(Cn + C_H)}{C(1 - n) - C_H}. \qquad (VI)$$

The calculated values of K_1 for a portion of the data are given in column 4 of Table III.

If in addition to the equilibrium of equation (I) that of equation (II) is involved, the equilibrium

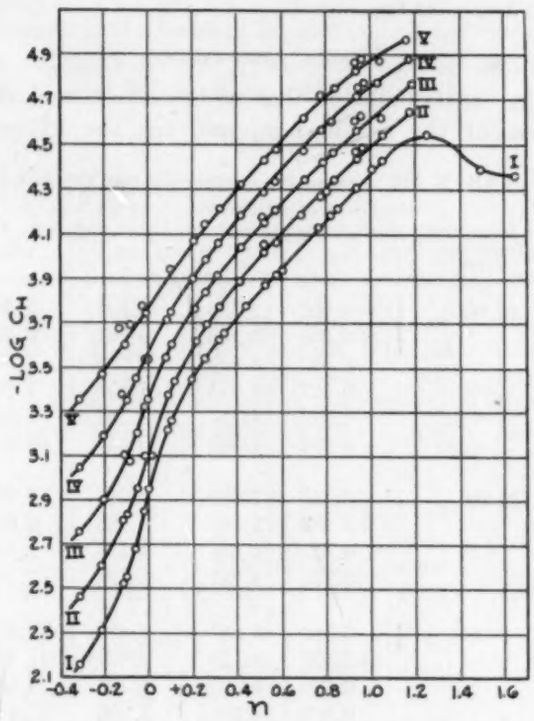


FIG. 3. Acidity of scandium perchlorate solutions at $t = 25.0°C$, $\mu = 1.00_0$. 10^3C = curve I—20.0_0; curve II—10.0_0; curve III—5.0_0; curve IV—2.50_0; and curve V—1.25_0.

TABLE II. *Coefficients for equation (V)*

Temp °C	Total conc. Sc	A	B	Mean dev. in $-\log C_H$
	moles/liter			
25	2.00×10^{-2}	3.262	1.131	0.0066
	1.00×10^{-2}	3.425	1.098	0.0060
	5.00×10^{-3}	3.582	1.078	0.0065
	2.50×10^{-3}	3.711	1.088	0.0076
	1.25×10^{-3}	3.875	1.052	0.0115
40	1.00×10^{-2}	3.179	1.069	0.002
	1.25×10^{-3}	3.648	0.968	0.014
10	1.00×10^{-2}	3.745	1.050	0.005
	1.25×10^{-3}	4.187	1.022	0.012

constants K_1 and K_2 can be calculated from the relationship

$$\frac{C_H(Cn + C_H)}{C(1 - n) - C_H} = K_1 + \frac{C(n - 2) + C_H}{C_H[C(1 - n) - C_H]} K_1 K_2. \qquad (VII)$$

Best values of K_1 and K_2 were calculated by linear regression methods yielding values of 4.39×10^{-4} and -3.19×10^{-6}. Substitution of K_2 back in equation (VII) yields the numbers given in column 5 of Table III. The values in columns 4 and 5 are not constant, indicating that neither treatment is satisfactory. The same statement can be made in regard to a triprotic treatment.

Dimer Treatment

On the assumption that equations (I) and (III) represent the equilibrium, one has the following

TABLE III. *Test of the monoprotic and diprotic acid postulates*

Total conc. Sc 10^3C	n	$-\log C_H$ exp	10^4K_1	10^4K_2
20.00	−0.307	2.152	3.347	3.351
	+0.093	3.256	0.761	0.815
	0.327	3.620	1.230	1.377
	0.527	3.874	1.530	1.860
	0.827	4.187	3.180	4.666
	0.993	4.394	80.64	69.5
10.00	−0.213	2.603	0.945	0.956
	+0.260	3.694	0.788	0.954
	0.527	4.008	1.138	1.589
	0.787	4.285	1.978	3.548
5.00	−0.107	3.087	0.492	0.527
	+0.527	4.156	0.823	1.461
	0.780	4.425	1.393	3.523
	0.934	4.591	3.956	13.48
2.50	−0.0100	3.544	0.332	0.435
	+0.260	3.991	0.439	0.775
	0.527	4.293	0.616	1.499
	0.933	4.711	3.090	15.99
1.250	−0.307	3.351	0.232	0.297
	+0.260	4.134	0.344	0.815
	0.527	4.435	0.461	1.703
	0.827	4.739	0.969	6.59
	0.949	4.878	3.145	30.41

mathematical relationships relating concentration of species

$$C = C_3 + C_2 + 2C_{2,4} = \frac{1}{a} C_{ClO_4^-} \quad \text{(VIII)}$$

where C_3, C_2, and $C_{2,4}$ represent the concentrations of Sc_3, Sc_2, and $Sc_{2,4}$ and

$$3C_3 + 2C_2 + 4C_{2,4} + C_{NaOH} + C_H = aC + C_{HClO_4} \quad \text{(VIIIa)}$$

and

$$K_0 = C_H^2 C_{2,4}/C_3^2 = K_1^2 K_D \quad \text{(IX)}$$

where K_D is the equilibrium constant for equation (III) and K_0 is an over-all constant for the equilibria of (I) and (III). From the above, introducing equation (IV), one may derive the expression

$$\frac{C_H(Cn + C_H)}{C(1-n) - C_H} = K_1 + \frac{2[C(1-n) - C_H]}{C_H} K_0 \quad \text{(X)}$$

and this equation may be written in the form

$$C_H^3 + C_H^2 (Cn + K_1 - 2K_0) + C_H[C(1-n)(4K_0 - K_1)] - 2K_0[C(1-n)]^2 = 0. \quad \text{(XI)}$$

On substituting measured values of C, C_H, and n into equation (X) one derives equations of the form $A = K_1 + BK_0$, where A and B are pure numbers. While such an equation can be derived from the data for each individual buffer studied, it is obviously necessary to group the data at least into pairs of equations in order to evaluate K_1 and K_0. We have felt it preferable to group the equations into sets of five, each such data group consisting of the equations derived from buffers at essentially the same values of n, but for each of the five scandium concentrations studied. The resulting groups of five

TABLE IV. *Test of the dimer postulate*

Data at $t = 25°C$, $\mu = 1.00_0$, primarily $NaClO_4$

Data group	Approx. values of n	Best values of the constants			
		10^4K_1	10^4K_0	$10^{-3}K_D$	$10^{11}K_1K_3$
1	−0.0100	0.842	1.683	13.80	1.420
2	+0.103	1.1$_7$2	1.016	7.38	1.190
3	0.209	1.383	0.916	4.78	1.266
4	0.527	1.685	0.978$_5$	3.45	1.648
1 and 2		2.035	0.901	2.17$_6$	1.825
1, 2, and 3		1.865	0.957	2.75$_2$	1.785

equations when solved simultaneously by linear regression methods, lead to the values of K_1 and K_0 and thence to K_D by equation (IX), which are summarized in Table IV. The resulting sets of constants should be identical and independent of the method of grouping data. Table IV shows that this is not the case and, furthermore, combinations of the various groups of data do not yield average values.

Nevertheless, a further examination of the postulate was made by choosing a value of K_1 and K_0 from Table IV, substituting this value in equation (XI) and comparing the calculated values of hydrogen ion concentration with those determined experimentally. Table V presents the comparison for $K_1 = 1.17_2 \times 10^{-5}$ and $K_0 = 1.01_6 \times 10^{-6}$ for stoichiometric concentrations of scandium from 2×10^{-2} to 1.25×10^{-3}, and at $t = 25°C$, $\mu = 1.00_0$. Comparison of experimental and calculated values indicates good agreement up to $n = 0.5$; the mean deviation for $n < 0.5$ is 0.026 log units. The results for one set of buffers are shown graphically in Fig. 4, which is typical for all graphs of the data. Fig. 5

shows a comparison between the titration data employed to establish a values, and the curve calculated from equation (XI). It appears that the postulated equilibria of equations (I) and (III) enable one to predict the values of the hydrogen ion concentration over the range of n values indicated.

Continuous Polymerization

Returning to the linear relationship between $-\log C_H$ and n in the region $n = 0.3$ to 1.0, it should be noted that the dependence of C_H on n can be expressed only by an exponential function and no simple power series of the type employed above can explain the data over the entire range of n values. However, by employing the first few terms of such a series, we have been able to reproduce the experimental values of hydrogen ion concentration over a limited range of n values.

From the standpoint of the structural chemistry involved, it follows that the degree of aggregation of the scandium species in solution must increase as n increases, passing through dimer, trimer, tetramer, and higher stages of aggregation. This concept has been applied with considerable success by Graner and Sillén (6) in their study of bismuth perchlorate systems. Calculations based on various postulates of polymerization involving oxygen or hydroxy bridges indicate that the data at high values of n are consistent with the idea of continuous polymerization, but no definite quantitative conclusions can be drawn.

Accepting the concept of continuous polymerization, values of K_1 and K_0 calculated as above must depend on n since other equilibria beyond those of equations (I) and (III) become increasingly important as n increases. On this basis, values of the constants should be calculated at the lowest values of n studied. Analysis of the derivatives dC_H/dn, dC_H/dK_1, dC_H/dK_0, as well as the second derivatives, indicates that the calculated values of C_H are most sensitive to changes in K_1 and K_0 at $n = 0$. However, at $n = 0$, experimental uncertainties in C and n are at a maximum. As a compromise, we have employed constants calculated at $n = 0.1$ in examining the equilibria proposed above.

Considerable data were also obtained at $t = 10°C$

TABLE V.

$-\log C_H$ for Sc buffers at $t = 25.0°C$, $\mu = 1.00_0$

C	$2.00_0 \times 10^{-2}$		$1.00_0 \times 10^{-2}$		5.00×10^{-3}		2.50×10^{-3}		1.25×10^{-3}	
n	exp	calc	exp	calc	exp	calc	exp	calc	exp	calc
−0.307	2.152	2.208	2.460	2.505	2.752	2.797	3.054	3.086	3.351	3.365
−0.207	2.312	2.373	2.604	2.665	2.901	2.949	3.192	3.223	3.466	3.484
−0.107	2.530	2.624	2.818	2.893	3.087	3.149	3.358	3.393	3.600	3.624
−0.067	2.675	2.761	2.942	3.028	3.196	3.242	3.463	3.466	3.697	3.684
-0.010_0	2.933	2.972	3.105	3.175	3.343	3.375	3.544	3.572	3.747	3.768
+0.083	3.218	3.235	3.387	3.397	3.555	3.562	3.731	3.731	—	—
+0.103	—	—	—	—	—	—	—	—	3.934	3.928
0.193	3.451	3.434	—	—	—	—	—	—	—	—
0.209	—	—	3.618	3.609	3.769	3.758	3.905	3.912	4.083	4.066
0.260	3.559	3.531	3.694	3.680	3.846	3.829	3.991	3.979	4.134	4.128
0.327	3.620	3.619	3.777	3.768	3.919	3.915	4.055	4.062	4.202	4.209
0.419	—	—	3.890	3.883	4.033	4.029	4.171	4.175	4.319	4.319
0.456	3.785	3.782	—	—	—	—	—	—	—	—
0.527	3.874	3.873	4.011	4.021	4.161	4.167	4.291	4.311	4.435	4.455
0.577	3.911	3.941	4.047	4.089	4.201	4.239	4.330	4.379	4.473	4.522
0.696	—	—	4.187	4.368	4.339	4.418	4.478	4.562	4.627	4.705
0.761	4.130	4.250	—	—	—	—	—	—	—	—
0.827	4.187	4.408	4.339	4.555	4.470	4.701	4.602	4.845	4.739	4.987
0.934	4.316	4.853	4.452	5.000	4.591	5.146	4.735	5.290	4.861	5.432
1.033	—	—	4.524	5.347	4.628	5.502	4.774	5.660	4.866	5.820
1.043	4.428	5.080	—	—	—	—	—	—	—	—
1.181	—	—	4.660	4.636	4.766	4.791	4.880	4.949	4.968	5.104
1.243*	4.542	4.365	—	—	—	—	—	—	—	—
1.493	4.389	4.097	—	—	—	—	—	—	—	—
1.642	4.372	4.003	—	—	—	—	—	—	—	—

* Precipitation of scandium occurred at this and higher values of n.

and 40°C, and at ionic strengths of 0.500, 0.100_0, and 0.0100_0. These data, treated in the manner discussed above, led to dissociation and dimerization constants under the conditions indicated, the resulting calculated values of $-\log C_H$ agreed as well with experimental values as above. These data plus the associated values of ΔH, ΔS, and ΔCp for the processes involved will be the subject of a later paper.

Significance of the Results

It has been shown that the hydrogen ion concentrations of scandium perchlorate systems cannot be represented by equilibria involving simple proton dissociations as the systems are complicated by the formation of polymeric species. However, the hydrogen ion concentrations of these solutions can be represented over a broad range of concentrations and buffer ratios by assuming only two equilibria to be of importance. These are the acid dissociation of the aquoscandium ion and a dimerization of the conjugate base of the aquo acid. The assumed equilibria are consistent with data obtained at 10°, 25°, and 40°C at ionic strengths 1.00, 0.500, 0.100, and 0.0100 where the solvent salt is sodium perchlorate in swamping concentration.

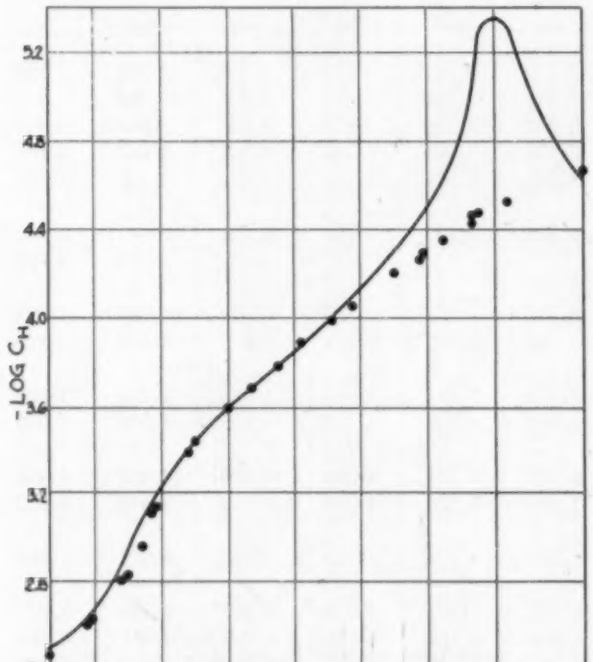


Fig. 4. Acidity of scandium buffers at $C = 1.00_0 \times 10^{-2}$ M, $t = 25.0$°C, $\mu = 1.00_0$. Solid curve calculated from dimerization equilibrium constants; closed circles are experimental points.

The results of the study provide a physical picture of the processes which occur in solution as hydroxide is added to aqueous solutions of aquo ions.

It is proposed that the scandium species present in largest concentration in scandium perchlorate solutions is the Sc_3 species. Complexes with perchlorate are presumed not to exist nor are complexes other than hydroxy complexes possible in the systems containing only $Sc(ClO_4)_3$, NaOH, $HClO_4$, and $NaClO_4$. The Sc_3 ion, by interaction with the solvent in the Brönsted sense, undergoes acidic dissociation to produce the Sc_2 species, as in equation (I).

$$Sc_3 + H_2O \rightleftarrows Sc_2 + H_3O^+ \qquad (I)$$

Under ordinary conditions, that is, in solutions of the normal perchlorate which do not contain added base, reaction (I) would not proceed very far to the right if only equilibrium (I) occurred in the solution. This statement follows from the low values of

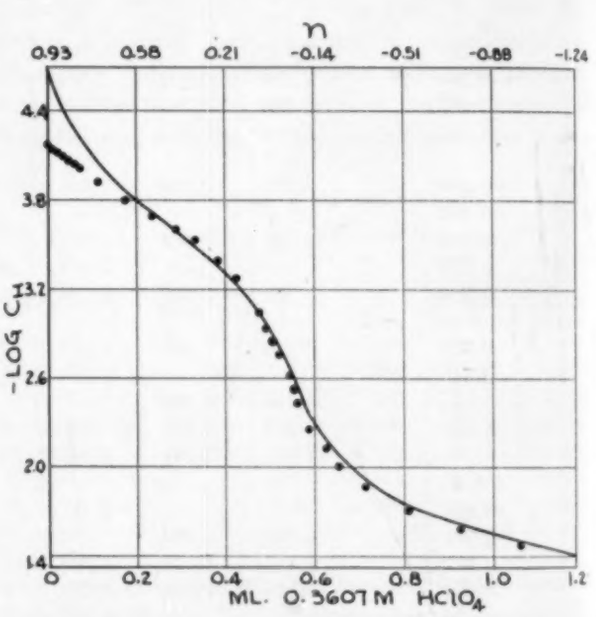


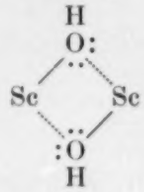
Fig. 5. Titration of 0.0400M $Sc(ClO_4)_3$. Solid curve calculated from dimerization equilibrium constants; closed circles are experimental points.

K_1, found in this study to be of the order of 10^{-4}. However, a second reaction occurs; the Sc_2 species formed in equation (I) dimerizing as indicated in equation (III)

$$2Sc_2 \rightleftarrows Sc_{2,4} \qquad (III)$$

Since the dimerization constant for this reaction is quite large—of the order of 5000 to 10,000—it follows that most of the Sc_2 species is effectively removed from the solutions by the dimerization reaction. Consequently, reaction (I) is shifted to the right much more than would be the case if no dimerization occurred. It would appear that the dimerization process is strongly temperature-dependent, and may be accompanied by large positive entropy changes.

From the standpoint of the structural chemistry involved, the structure of the dimer is probably



where the groups other than hydroxyl in the coordination sphere of the scandium are omitted for the sake of simplicity.

The presence of two hydroxyl groups in the bridge, while perhaps not necessary for the formation of a dimer, seems nevertheless to be necessary for the formation of a dimeric species of sufficient stability to be of importance in the equilibria. This statement follows from the fact that the dimerization postulate employed here is successful in reproducing the C_H values of the solutions studied. If the intermediate species $Sc_{2,5}$ were present in the solutions in concentrations of the same magnitude as Sc_2 or $Sc_{2,4}$ it seems very unlikely that the calculations could have been successful.

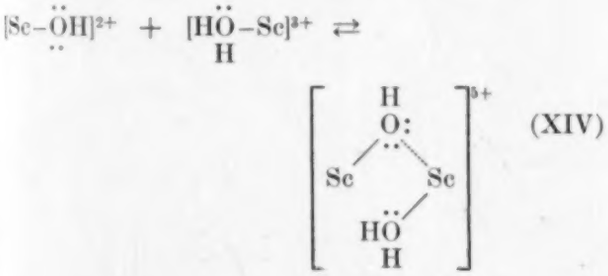
On the other hand, it must not be supposed that the monohydroxy discandium species is completely insignificant in these postulates. Thus, if a mechanism were to be proposed for the dimerization, it might be in terms of the following series of reactions:

$$Sc_3 + H_2O \rightleftarrows Sc_2 + H_3O^+ \qquad (I)$$

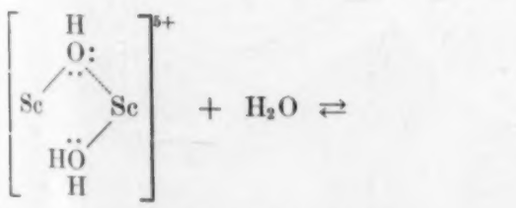
$$Sc_3 + Sc_2 \rightleftarrows Sc_{2,5} \qquad (XII)$$

$$Sc_{2,5} + H_2O \rightleftarrows Sc_{2,4} + H_3O^+ \qquad (XIII)$$

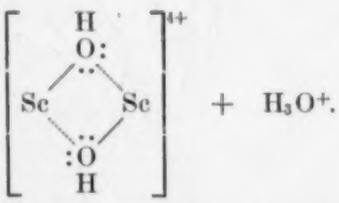
or, rewriting (XII) and (XIII) structurally:



(XIV)

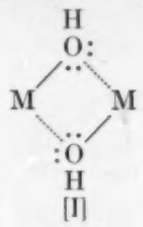


(XV)

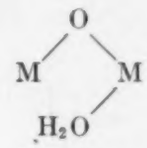


The greater stability of the dihydroxy dimer as compared with the monohydroxy species, proposed here, could be explained readily on the basis of the great increase in resonance energy which must accompany formation of the dihydroxy bridge as a consequence of the equivalent structures of the hybridized forms in the latter case only.

The proposals above differ from those of Graner and Sillén (6) primarily in that hydroxy rather than oxo bridging is proposed here. It is not possible by experimental techniques available at present to distinguish between the two types of ions proposed in the dispersed phase, namely,



[I]



[II]

Since species [I] is undoubtedly readily converted to [II] and vice versa, by general acid-base reaction with the solvent water, there is no major difference between the two proposals, as far as the dispersed phase is concerned. However, it is felt that the proposal of dihydroxy bridges better reflects the steps by which the polymerization occurs initially. The distinction between oxy and diol links, if real, is probably unimportant until the degree of polymerization approaches that of the insoluble species.

Finally, by extending the ideas proposed here, we may explain the eventual formation and precipitation of solid polymers from the scandium systems. We propose that the $Sc_{2,4}$ species can go on to form higher molecular weight polymers by an almost infinite number of different mechanisms involving, at least initially, formation of additional dihydroxy bridges. Thus one may write the sequence of steps:

$$Sc_{2,4} + H_2O \rightleftarrows Sc_{2,3} + H_3O^+ \qquad (XVI)$$

followed either by

$$2Sc_{2,3} \rightleftarrows Sc_{4,6} \qquad (XVII)$$

or by

$$Sc_{2,3} + Sc_2 \rightleftarrows Sc_{3,5}, \text{ etc.} \qquad (XVIII)$$

The addition of base to the scandium solutions would be expected to result in increasing the average number of coordinated OH^- groups per scandium, which in turn determines the extent of the polymerization. The process is terminated with formation of species whose solubility is so low that precipitation occurs.

The entire situation is very much more complex in the presence of anions, other than perchlorate, which may form complexes with the metal ions since

under these conditions there must be a competition between the anions, water, and OH^- for the available positions in the coordination sphere of the metal ion. The insoluble species formed on the addition of base will, in these cases, depend on the stability of the coordinate bond between metal ion and complexing anion. Considerable experimental data concerning this phenomenon in hydrous alumina systems may be found in the paper by Clay and Thomas (2).

Acknowledgment

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Any discussion of this paper will appear in a Discussion Section, to be published in the December 1953 issue of the JOURNAL.

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